THE AMERICAN JOURNAL OF SCIENCE.

EDITOR: EDWARD S. DANA.

FOURTH SERIES

VOL. XXXV—[WHOLE NUMBER, CLXXXV].

NEW HAVEN, CONNECTICUT.
1913.

THE TUTTLE, MOREHOUSE & TAYLOR COMPANY
NEW HAVEN

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VOL. XXXV. JANUARY, 1913.

Established by **BENJAMIN SILLIMAN** in 1818.

THE
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No. 205—JANUARY, 1913.

NEW HAVEN, CONNECTICUT.
1913.

THE TUTTLE, MOREHOUSE & TAYLOR CO., PRINTERS, 123 TEMPLE STREET.

Published monthly. Six dollars per year, in advance. $6.40 to countries in the Postal Union; $6.25 to Canada. Remittances should be made either by money orders, registered letters, or bank checks (preferably on New York banks).

THE

AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

Art. I.—*Glacial Cirques near Mount Washington;* by J. W. Goldthwait.

Among the unsettled problems of glacial history in New England, none is more inviting than that of extinct local glaciers. Yet it is true that in the last thirty or forty years no problem has been more neglected. It is natural that our early glacialists, eager to find phenomena in this country similar to those which had been described by Louis Agassiz in the Alps, and coming directly under the personal influence of that great originator of the theory of an Ice Age, saw in the White Mountains many features which they attributed to local glaciers rather than to the "drift agency." But with the rapid progress in glacial studies throughout the country and the growing recognition of the various types of topographic and geologic evidences of the continental ice sheet, the conception of mountain snowfields and valley glaciers was gradually put aside and all but forgotten. There is no question that some of the alleged evidences of local glaciers in northern New England which these pioneers in glacial geology presented are faulty, and deserved the obloquy into which they fell. Local deflection of the movement of ice in the ice sheet where it followed deep valleys will explain many a groove and scratch which these early glacialists assigned to valley glaciers. Kame building against lingering tongues of stagnant ice now explains many ridges and mounds which even to the most experienced glacialists of the earlier generation seemed accountable only as the terminal moraines of valley glaciers. Nevertheless it is strange that while investigators have been working out with great care and in great detail the records of local Pleistocene glaciers on ranges of the Rockies and Sierras, no one has searched for similar evidences on the highest mountain in the eastern part

Fig. 1.

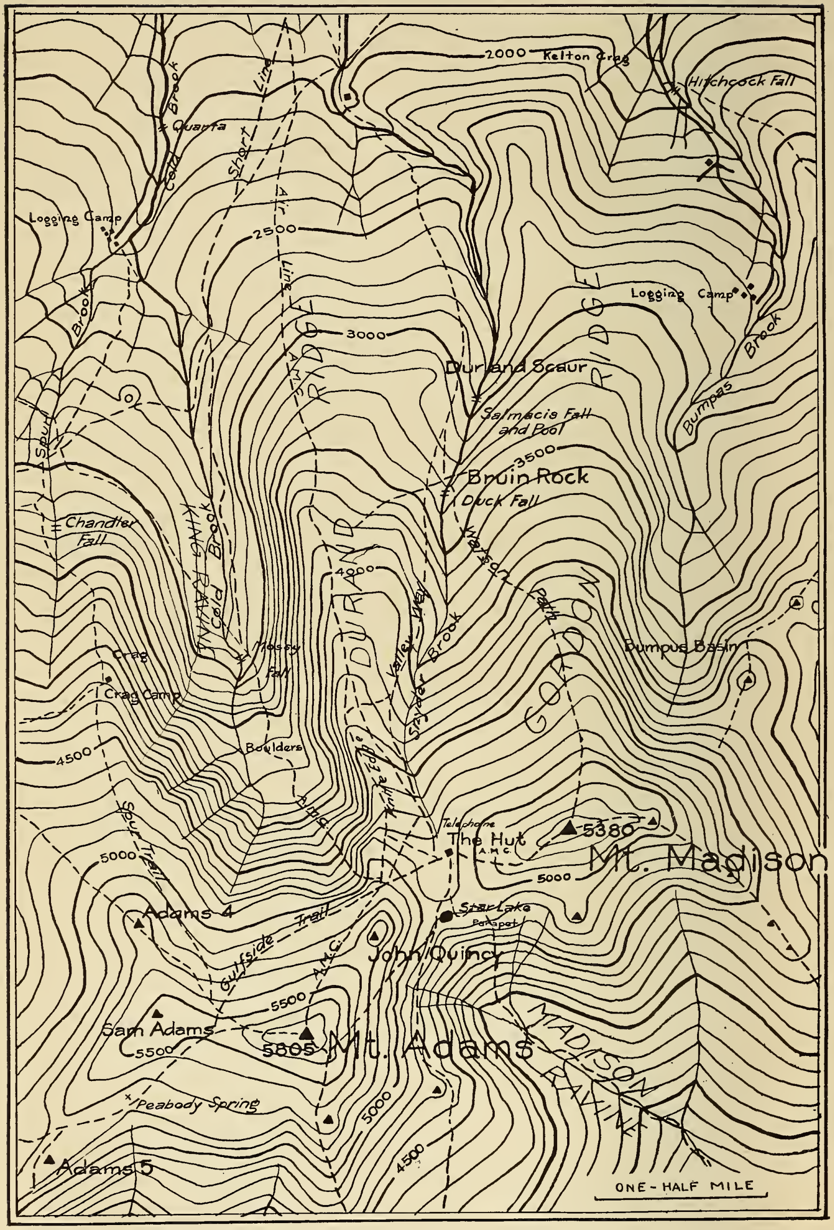

Fig. 1. Contour map of the ravines around Mounts Adams and Madison. Taken from Mr. Louis F. Cutter's "Map of the Northern Peaks," published by the Appalachian Mountain Club in 1911. Contour interval, 100 feet.

of the glaciated region. On Mount Washington, if anywhere in the eastern states, one would expect to find evidences of local glaciers which developed in the shelter of its summit before the ice sheet, spreading southward from Canada, reached and enveloped the White Mountains, or which, when the ice sheet melted away, lingered for a time in spite of the return of a more temperate climate.

Tarr's study of the glaciation of Mount Ktaadn in northern Maine in 1899* stands alone as the product of a modern physiographer and glacialist working in the mountainous interior of New England. In this paper Tarr stated reasons for the belief that this isolated mountain, inferior to Mount Washington in altitude, and buried, like it, beneath the ice sheet, was subsequently occupied "as a last stage of ice action" by local glaciers, which filled several basin-shaped valleys and built well-defined moraines. The evidences given were: (*a*) the fresh, unweathered appearance of the precipitous valley walls, which, although lacking glacial polish, are so much smoother than the rock-strewn table land above them as to suggest that valley glaciers have only recently withdrawn from them, just as to-day they are melting out of certain valleys on the coast of Greenland; (*b*) "bear den" moraine deposits on the floors of the steep-walled valleys or "basins," described as hummocky, with kettles occupied with ponds, and strewn with blocks which have come almost exclusively from the crags above. Associated with this morainic accumulation Tarr noted what seemed to be a lateral and an imperfectly formed medial moraine in the "North Basin," although on account of the density of the scrub forest close inspection of the ridges was impossible. "I should not wish to pronounce it positively a lateral moraine," he wrote, "though I fail to see any other explanation for it;" (*c*) a high ridge of rock debris which extends in front of the mouths of two valleys, as a terminal moraine might be expected to do.

So far as I know there has been hitherto no such study of the Presidential Range as this study of Mount Ktaadn by Tarr. The early glacialists, although reporting valley moraines, northwestward moved erratics, and locally controlled striæ in the lower, outer parts of the White Mountains, seem to have neglected to look for confirmatory evidence on the ranges from which such glaciers must have been fed. It is true, of course, that little attention was given in those days to the forms of mountain sculpture peculiar to alpine glaciers. Otherwise it is probable that the peculiar "gulfs" or "ravines" of the Presidential Range would have been appreciated forty years ago, as

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*R. S. Tarr: Glaciation of Mount Ktaadn, Maine, Bull. Geol. Soc. America, xi, pp. 433–448, 1900.

records of extinct White Mountain glaciers, instead of being ascribed to "the action of frost, gravity and water power."*

With much skepticism as to the existence of local glaciers in the lower, outer portion of the White Mountains region as reported by others, yet with a growing conviction, based on photographs and maps, that satisfactory evidences of local glaciers might be found near Mount Washington, I made plans last summer for a field study of this problem. Accompanied by Mr. Fred B. Plummer, a graduate student at Dartmouth College, and Mr. W. Lee White, Dartmouth 1912, I spent six weeks on and around the "Northern Peaks" of the Presidential Range, gathering physiographic and geologic data, collecting photographs, and constructing a topographic map of two of the ravines. So far as our observations bear directly upon the local glaciation of the range by valley glaciers they will be briefly sketched in the pages which follow. The conclusions reached are: that prior to the advance of the continental ice sheet over the White Mountains, either early in the last glacial epoch or during a still earlier epoch, the Presidential Range was covered by a snow field from which for a considerable time several vigorous valley glaciers were nourished; that the range later became completely buried by the ice sheet from Canada; and that upon the final melting away of the continental ice from the mountains in question, the local glaciers did not again come into existence. In this last respect our conclusions contradict not only the opinion held by Agassiz, Hitchcock and other early investigators in New Hampshire, but that held by Tarr in Maine.

It would be unfitting even in so short a paper to fail to acknowledge the aid which I have received in this field work from the Appalachian Mountain Club, whose scores of well constructed mountain trails and paths have made the range easily accessible and whose readiness to further any form of scientific work which reveals new facts of natural history in these White Mountains I am not the first to appreciate. I am indebted also to Mr. Guy Shorey of Gorham, N. H., for the use of the three photographs which accompany this paper.

General Physiographic Description of the Presidential Range.

The Presidential Range is a crooked and broken line of mountains that extends from Randolph, New Hampshire, southward about twenty miles to Bartlett. Mount Washington, the dominating summit, with an altitude of 6,293 feet, stands about midway between the two ends of the range. When viewed from one of the summits, the general surface of

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*C. H. Hitchcock: Geology of New Hampshire, vol. i, p. 623, 1874.

the range is seen to be a gently swelling and sagging upland, hardly flat enough to call a table land or plateau, yet with slopes so gradual as to excite attention from even a casual visitor. The smooth "lawns" from which the several conical summits rise gradually several hundred feet, find extension in many places down the flanks of the range in graded spurs or "ridges" which separate the deep "ravines" or "gulfs." These profound hollows in the sides of the range, heading sharply in crescentic precipices and stretching forward as broad U-shaped troughs, are the dominant features of the range, adding greatly to the impression of height which one gets when viewing the mountains from below. If such "gulfs" occur at all on the lower ranges of the White Mountains, they are at least less striking there than on the Presidential Range.

The greater part of the undulating upland is a bare gray desert of loose rock and rifted ledges. Only its lower stretches are invaded by the dense scrub of fir and spruce. The continuity of this upland surface across the saddles or cols of the range from cone to cone, and the accordance of its surface on opposite sides of the great ravines indicate, as Hitchcock and others long ago recognized, that it originally extended over the entire range and was interrupted only by the subdued mountain summits. The intricately contorted structure of the schists which compose the range indicates that the smooth upland represents a vast amount of denudation, whereby the original lofty mountains were reduced to broad, gently sloping forms, surmounting a peneplain of great extent. The presumption is that this is to be correlated with the Cretaceous peneplain of southern New England.* The ravines have been hollowed out of it since a general uplift of the region, first by normal weathering and stream erosion and later by valley glaciers. Foreign bowlders mingled with the loose rock of the upland surface, polished and striated surfaces of vein quartz, and other evidences of glaciation up even to the summits of Mounts Jefferson, Adams and Washington, indicate, as Hitchcock discovered in 1875, that the continental ice sheet completely buried the range. Naturally certain changes of slope and outline are to be attributed to this regional glaciation; but these are much subordinate to the other features. In a sentence, then, this range may be described as an irregular line of subdued domes or cones, formed during a cycle of denudation which baselevelled southern New England, but failed to remove mountains here at the headwaters of the New England rivers, subsequently raised, with the rest of New England, and dissected on all sides by rejuvenated mountain torrents, then

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*W. M. Davis: The Physical Geography of Southern New England. National Geographic Monographs, No. 9, 1895.

snow-covered and carved by valley glaciers, and at length given certain minor alterations by the continental ice sheet.

The "Gulfs" or "Ravines."

The abnormal size and shape of the ravines which so deeply indent the sides of the Presidential Range has been commented on by many writers. It would be hard to find a more vivid description of them than was written by Starr King, for whom one of the grandest of the gulfs has been named. Telling of a trip up Tuckerman Ravine, he says:

> "Emerging from the woods now, we see that the ravine is of horseshoe shape, the opposite outer cliff more than a thousand feet in height, the bottom sloping upwards towards the backward crescent wall and the rim quite level. . . . . Facing us as we climbed was the grand curve of the precipice, symmetrical seemingly as that of the great Colosseum. . . . . The face of the wall was wet with weak streams that flash brilliantly in the sun. . . . . The stupendous amphitheatre of stone would of itself repay and overpay the labor of the climb. It is fitly called the 'Mountain Colosseum.' No other word expresses it; and that comes spontaneously to the lips. . . . . The eye needs some hours of gazing and comparative measurement to fit itself for an appreciation of its scale and sublimity. One can hardly believe while standing there, that the sheer concave of the back wall of the ravine was the work of an earthquake throe."*

In Professor Hitchcock's "Geology of New Hampshire," references appear over and over again to the peculiar form of these great ravines, which have been "hollowed out of the mountains." From the empyrical descriptions one comes to suspect that the gulfs owe their broad form and crescentic headwalls to valley glaciers. Several line drawings borrowed from Starr King's "White Hills" lend weight to this suspicion, particularly one view of King Ravine from Randolph Hill.† In describing Tuckerman Ravine, Hitchcock calls it a deep cleft, near the foot of Mount Washington, "excavated out of the plateau much in the manner of a gorge." The descent into it from the plateau "is dangerous along the most feasible route, and impossible most of the way. The innermost part of the ravine is semi-circular, the outer cliff rising directly a thousand feet." Farther down, as it approaches the Glen, "the gorge becomes more open and is hardly to be distinguished from ordinary mountain valleys."‡ Accompanying this description is a remarkably good heliotype which shows the

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*T. S. King: The White Hills, their legends, landscape, and poetry. Boston, 1860, pp. 346-349.

† C. H. Hitchcock: Geology of New Hampshire, vol. i, fig. 81, 1874.

‡ Op. cit., pp. 622-624.

Fig. 2.

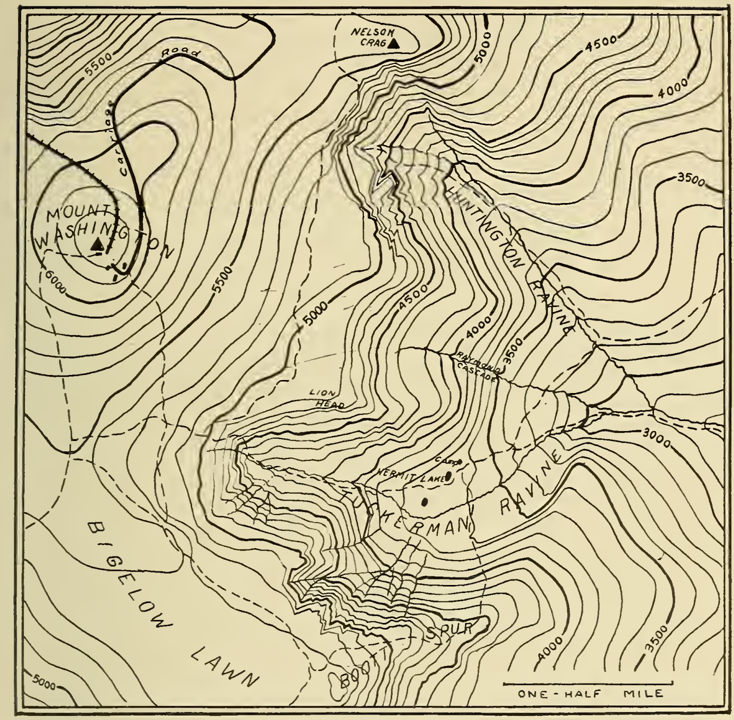

Fig. 2. Contour map of Huntington and Tuckerman Ravines. Same scale and contour interval as in fig. 1. Made by the author in August, 1912.

sharp semicircular rim of the ravine, at the foot of Mount Washington. Altogether, the picture that one gets from a modern reading of Hitchcock's report is that of a range whose smooth sides have been grooved or channeled by glaciers. To one accustomed to look to physiographic evidence to support the theory of local glaciers of the Alpine type, it seems strange that Agassiz and Hitchcock, enthusiastic advocates of the local glaciation of the White Mountains, did not seize upon the cirque form of these well-known ravines to more fully substantiate their belief.

Although close scrutiny of the photographs accompanying the present paper will, I think, satisfy many that no agency except valley glaciers can have produced these peculiar ravines, it is worth while, in view of other possible hypotheses, to consider what facts in addition to the trough-like form and semicircular heads of these ravines must be accounted for. Two facts, in particular, are made clear by the contour maps:

(*a*) the ravines or gulfs lie on all sides of the range, and trend in all directions. Those which we visited and studied last summer have the following courses:

Ravine of the Castles	N. 50° W.
King Ravine	N. 20° W.
Bumpus Basin	N. 10° E.
Madison Ravine	S. 50° E.
Jefferson Ravine	S. 75° E.
Great Gulf	N. 35° E.
Huntington Ravine	S. 40° E.
Tuckerman Ravine	S. 80° E.
Gulf of Slides	due east.

Several ravines southwest of Mount Washington, seen only from a distance and not yet mapped with sufficient care to give assurance of their glacial origin, seem to be cirques; likewise Oakes Gulf, south of Mount Washington, which trends southward.

(*b*) Side by side with these gulfs, on the slopes of the range, are one or two typical torrent-carved valleys. Perhaps the most striking example is the valley of Snyder Brook, which descends the northern end of the range, midway between King Ravine and Bumpus Basin. In his contour map of the "Northern Peaks," published by the Appalachian Mountain Club, Mr. Louis F. Cutter has brought out with great fidelity the contrast between this narrow ravine, which bends from side to side several times during its steep descent, and the broad, straight, steep-walled trough which lies beside it. These two ravines are utterly unlike in shape and size; and yet they are occupied by streams approximately equal in volume, and in their ability to transport whatever material is delivered to them. The process which has so clearly broadened King Ravine, trimming away the intervening spur, Durand Ridge, to form the "Knife Edge," has not operated in the valley of Snyder Brook.

The Origin of the Ravines.

In his report of 1875, Hitchcock accounts for the peculiar shape of the ravine as follows:

> "Tourists are fond of imagining this and other ravines in the State as the product of some tremendous earthquake throe. They are more easily explained by the action of frosts, gravity, and water power. With the elevation of the mountains, there will naturally be a few lines of depression which give origin to streams. In the cooler season the water freezing in the seams of the rock will detach slabs and blocks of stone. These acted

upon by streams, will eventually be changed to gravel and sand, and be washed down the mountain, leaving fresh surfaces for the renewed winter freezing. In this way, little by little, the excavation goes on, the deep, ragged ravines notching the mountains where the formation happens to be slaty and permeated with numerous joints." *

FIG. 3.

FIG. 3. King Ravine and Mt. Adams from Randolph. Photograph by Shorey. In the floor of the cirque may be seen the great pile of blocks stretching forward from the foot of the headwall.

It is true that the foliation planes and well-developed joints of the mica schists of the Presidential Range permit frost and gravity to act very effectively on the steep ravine walls. A study of the joints in these ravines fails, however, to disclose in them any satisfactory reason why the ravine heads should have grown semicircular. The joints do not run in a wide arc like that made by the crescentic rim of the cirque; they run in the usual way, in systems which are straight for long distances and which intersect obliquely, yielding polyhedral blocks. It is hard to see why the side walls of the ravines should have been eaten back by frost so fast, almost keeping pace with the recession of the headwalls, for the declivity of the side of the mountains is very considerable, and headward

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* Geology of New Hampshire, vol. i, p. 623.

growth ought greatly to exceed the lateral growth, unless the joints are so placed that they check the headward recession and promote lateral recession of cliffs at the ravine heads. So far as we could see, in our examination of the joint planes, no such influence is apparent. A second objection to this theory of the origin of the ravines lies in the presence so close together of the two contrasted types of valley, the narrow-headed V-shaped gorge and the bowl-shaped trough. Take for example the case of Snyder Brook valley and the two gulfs between which it lies. If Cold Brook, aided by frost and landslides, could have eaten out the great amphitheater which lies at the head of King Ravine, Snyder Brook, which is approximately equal to Cold Brook in volume, ought to have done a similar piece of work. There is no reason to suppose that the mica schist at the heads of King Ravine and Bumpus Basin is any more favorably jointed or more easily eaten out than that around the head of Snyder Brook. To attribute the difference between Snyder valley and the two troughs to abnormal jointing lays upon him who would urge

Fig. 4.

Fig. 4. View across the head of Tuckerman Ravine to Mt. Washington. Photograph by Shorey. The sharp rim and steep walls of the cirque are strongly contrasted with the subdued slopes of the cone of Washington and the surrounding lawn.

the theory the task of showing, by an intensive study of the district, what is abnormal about them. Further than this, close observation in the field is likely to lead one to doubt whether the original process of ravine wall recession is still going on. The cascades which fall over the headwalls bring down some loose material from the upland, chiefly stones from the ground moraine, and gather some waste from the exposed cliffs. Extensive cone-shaped "slides" of rock have collected at the foot of the crags, and hundreds of great blocks have fallen to the ravine floors; but these lie undisturbed and generally unaltered—they are not being "acted upon by streams" and "washed down the mountain" at anything like the rate at which the walls are being demolished. In other words, the rifting, sliding process which is going on to-day is tending not to maintain the declivity of these walls, but to reduce it; not to sweep clean the ravine floors, but to build them up.

Fig. 5.

Fig. 5. Headwall of Tuckerman Ravine in early summer. The snow arch lies just to the right of the center, where the brook which cascades down over the headwall makes its way beneath the snow drift. Piles of loose blocks are banked high against the foot of the walls on either side.

In view of the fact that the entire Presidential Range was at one time buried beneath the ice sheet, as Professor Hitchcock has proved,* it is worth while to consider whether the gulfs may not have been shaped by the movement of the continental ice. Undoubtedly there are instances in the White Mountains as elsewhere of valleys in which the ice sheet, chancing to move longitudinally, widened and straightened the preglacial river valleys, converting them into U-shaped troughs. The Crawford Notch and other notches may be examples of this sort. These, however, are "through valleys,"—deep saddles which connect the lowland on one side of a range with the lowland on the other side. The ravines around the Presidential Range, on the other hand, head boldly against the mountains in semicircular cliffs. Consider, for instance, King Ravine. It is hardly conceivable that the ice, pushing southeastward up King Ravine, would pluck blocks from its sides to the extent indicated by the excessive breadth of the trough, and at the same time, ascending its head, develop a cliff there which is almost equally precipitous. Such a headwall, rising twelve hundred feet at an angle of 45 or 50 degrees, would offer too great resistance to ice movements to be itself the product of regional glaciation. Other ravines, such as Huntington and Tuckerman Ravines, which, as just pointed out, trend southeastward, head in crescentic precipices similar to the headwall of King Ravine. Surely the ice which ascended King Ravine and then, passing across the col between Mounts Madison and John Quincy Adams, and descended into Madison Ravine would not have carved the heads of these opposed valleys in the same manner. It is equally improbable that the immense trough of the Great Gulf should have been excavated by the ice sheet, trending as it does almost perpendicular to the ice movement. One can see, indeed, in the contrast between the precipitous northwest side of the Great Gulf and the more moderate southeast side indication that the gulf form antedates the arrival of the ice sheet and has been somewhat modified by the transverse regional glaciation. Finally, the most vital objection to the ice sheet erosion theory of these ravines is that one or two valleys, like that of Snyder Brook, retain their narrow, crooked form, although they were in a position to suffer exactly the same widening, deepening, and straightening at the hands of the advancing ice as the neighboring ravines might suffer.

While thus the theory of abnormal jointing and frost action and the theory of ice sheet erosion fail to explain the ravines either singly or collectively, the remaining hypothesis—that of local glaciation by valley glaciers—presents no such difficulties.

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*C. H. Hitchcock: Existence of glacial action upon the summit of Mount Washington, N. H., Proc. Amer. Assoc. Adv. Sci., vol. xxiv, pp. 92–96, 1876.

As is well known, glaciers of the Alpine type widen the valleys which they occupy, converting them from winding V-shaped gorges into broad, straight, U-shaped troughs; by a quarrying process along the semicircular head crevasse or "bergschrund," they cut steep headwalls which grow back farther and farther into the mountain side. In their broader elements of form, King, Huntington, Tuckerman, and the other ravines already spoken of answer the description of true glacial cirques. In one other respect they seem to be characteristic. Although they are excavated in rocks of nearly uniform strength, their floors do not descend steadily, but by steps. In Tuckerman Ravine this is particularly noticeable about half a mile down from the headwall, where the pocket-like recess of the upper end opens into the wider, lower basin over a cliff which is fully fifty feet high. The presence of glacial cirques on all sides of the range is not surprising; indeed it is quite to be expected, although, as seems to be the case, there should be a greater development of them on the east side than on the west because of the lodgment of drifted snow on the leeward side. If these are stream valleys which have been deepened and widened by Alpine glaciers, it is not at all surprising that among them are a few normal V-shaped valleys like that of Snyder Brook, which, owing to their situation with reference to the drifting snows and protecting peaks, escaped the local glaciation which the others suffered.

The sculpture by these Mount Washington glaciers, although not extensive enough to develop perfect examples of lateral "hanging valleys," nevertheless approached that point. The glacier which widened the Great Gulf cut off the lower ends of several spurs of Mounts Clay and Jefferson, forming the great triangular "knees." Between the two knees of Jefferson is a hanging valley from which a stream cascades abruptly into the Great Gulf.

Age and extent of the valley glaciers.

Those writers who have presented evidence in favor of the existence of local glaciers among the New England mountains have invariably drawn the conclusions that these glaciers made their appearance after the withdrawal of the ice sheet, when local snow fields still occupied the higher summits. Most of the evidence which they offered is indeed capable of no other interpretation. Freshly formed terminal moraines such as Agassiz professed to find at Bethlehem,* northwestward striation reported by Professor Hitchcock, and similar surface markings could hardly have been made before the ice sheet

*Louis Agassiz: On the former existence of local glaciers in the White Mountains, Proc. Amer. Assoc. Adv. Sci., vol. xix, pp. 161–167, 1870.

appeared and have survived the strong regional glaciation. The cirque-like form of the basins on the side of Mount Ktaadn likewise was regarded by Tarr as the record of a "closing stage" of the glacial period. On theoretical grounds, however, Tarr conceived that there had been snow fields on the New England mountains during the coming on of the glacial period also, and that local glaciers had been nourished from several centers before the ice sheet reached this field. Indeed, he went further than this, and suggested that probably the glaciation of northern New England included (*a*) the development of local valley glaciers on the highest ranges; (*b*) the growth of these local snow fields into several local ice caps: (*c*) the period of continental glaciation, when the larger ice sheet from Labrador overwhelmed the smaller ice caps; (*d*) the re-establishment of local ice caps which spread both northward and southward from the International boundary, and (*e*) the disappearance of all save valley glaciers on Mount Ktaadn and the highest White Mountains. Without attempting to controvert the evidence of Agassiz, Hitchcock, and Tarr, which deserves detailed study in the field, I must point out that the facts observed last summer seem to show that although valley glaciers acted long and vigorously before the advance of the ice sheet into the White Mountains, they did not reappear when the ice sheet withdrew, or, at most, were comparatively insignificant. The reasons for this conclusion may now be briefly stated.

If the cirques in question had been excavated by valley glaciers in the closing stages of the ice age, one ought to find terminal moraines near the mouths or in the valleys beyond, and crescentic recessional moraines farther back, marking oscillations of climate during the final retreat of the glaciers. On the sides and floors of the ravines lateral and medial moraines might be expected.

We have seen that Tarr considered mounds and ridges of rock debris in the Ktaadn basins to be moraines, although the heavy forest which covered that country largely concealed the form of the ground. Much reliance was placed by him on the presence of lakes which seemed to be held in by moraines. In the more open and accessible ravines of the Presidential Range there is comparatively little difficulty in seeing and following the ridges and piles of rock waste. My expectation of discovering moraines in the ravines around Mount Washington, however, was not realized. The first surprise came when we commenced work, in King's Ravine. The upper end of this ravine, for half a mile between the headwall and Mossy Fall, is occupied by a mass of blocks, the outer edge of which is distinctly lobate. The blocks are all of mica schist like the rock in the headwall and side walls. At first sight this block-strewn floor looked promising. But we soon found that farther down the valley, in the half mile between Mossy Fall and its mouth, there is nothing in the form of the floor that suggests morainic topography. If this great cirque and trough had been filled by a valley glacier in the closing stages of the glacial period, its mouth should be encircled by a crescentic moraine, save where Cold Brook might have excavated it. The fact is, there is no such ridge of local debris. On the contrary, this lower floor is occupied by a thick sheet of typical ground moraine which is similar in composition to the till of the adjacent Randolph Valley, and which blends with it. A count taken of the pebbles in natural and artificial exposures of this till showed over 60% of material from outside the ravine,—much of it surely from the northwest, and less than 40% of the local mica schist. Striated, subangular pebbles are plentiful. The large bowlders are nearly all granites from the Crescent Range and Israel River Valley, a few miles northwest. Towards the side walls the ratio of local to foreign debris naturally increases; but over the greater part of the valley floor the southeast movement of the till is perfectly apparent. Forced by this evidence to admit that the lower half mile of the trough of King Ravine had not been occupied by a glacier since the disappearance of the ice sheet, we sought consolation in the block deposit above Mossy Fall, expecting to find there, at least, distinct records of a small, extinct glacier. Several days spent in clambering up and down over the blocks and in and out through the cavernous passages, and in viewing the deposits of floor and sides from all angles, left us very skeptical indeed as to the existence of even a short cirque glacier here subsequent to the departure of the continental ice sheet. That the huge mass of blocks came from the walls above is clear enough; but the fact that they seem to overlap the till deposit of the lower floor at Mossy Fall conveys the impression that the block mass is a later deposit than the till, and perhaps postglacial. On both sides of the ravine long talus cones or "slides" appear, some fresh, some covered with good-sized trees. They seem, however, to have little influence on the form of the block floor. One line of exceptionally large blocks followed by the "Subway trail" can be traced back to a prominent inclined joint face on the headwall. This resembles some of the rock falls described by Howe in the San Juan Mountains.* There are deep furrows or linear depressions among the blocks, especially near the foot of the side walls, yet the intervening ridges lack continuity too much to be regarded as recessional

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*Ernest Howe: Landslides in the San Juan Mountains, Colorado, including a consideration of their causes and their classification, U. S. Geol. Survey, Prof. Paper No. 61, 1909.

or lateral moraines. The lobate margin of the deposit, although suggestive of a convex glacier front, is equally well accounted for by the farther fling of avalanches from the headwall than from the sides,—indeed, it seems significant that on the headwall a system of joints which dips steeply, straight down the ravine, is widely exposed, as if large masses had been loosened and had fallen to the floor below. The block mass answers so well the description of the San Juan landslides that one is at once inclined to accept the explanation of post-glacial frost work and avalanches for it. There is, however, an objection to this. Some of the blocks are perched upon others, and in such high places that it seems impossible to account for their positions in any other way than by the melting out of solid ice from underneath them. The snow and ice which accumulate now in these ravines is neither thick enough nor solid enough to act as a toboggan slide for such heavy material, should it descend from the walls. At the time when the ice sheet was melting away from the range, however, avalanches might easily have descended on remnants of solid ice at the cirque heads; and the supply of loose blocks at that time must have been very plentiful, both because of the plucking action of the ice sheet, which had become well filled with joint blocks near the crags, and because of more intense frost action then than now. Stagnant masses of lingering ice of this kind, since they had no motion of their own, would leave no distinct moraines, merely a labyrinth of blocks; and that is what appears to be the case.

The same peculiar block deposits can be seen in Tuckerman Ravine, Huntington Ravine, the Great Gulf and the Ravine of the Castles. In the first mentioned ravine, around Hermit Lake there is a greater development than elsewhere of ridges of gravelly structure and kame-like habit. One of them curves half way around the lake, retaining an esker-like form for several hundred feet along the trail. Others near by seem to be composed of unwaterworn and unstratified debris. All are more or less irregular, without persistent or systematic trend or position. They are neither transverse nor longitudinal with respect to the valley, and although when viewed from a distance they seem to assume the form of looped moraines, they invariably prove on close examination to wander, split and disappear in a most inconsistent way. They are undoubtedly the kind of ridges described by Tarr in the Ktaadn basins. I am unable to see, however, that they are dependent at all on the presence of valley glaciers in these ravines. All that seems necessary to explain them is the presence for a while, in the closing stage of deglaciation, of stagnant ice of the waning ice sheet, in the shelter of the cirque walls, which received avalanche deposits and esker-stream gravels.

An interesting bit of confirmatory evidence of the antiquity of these valley glaciers is found in the asymmetry of the Great Gulf. There is no apparent reason why a valley glacier, occupying this gulf, should not have developed and left as steep a wall on the southeast side as on the northwest. Supposing, however, that the ravine was carved earlier in the glacial period and subjected to heavy glaciation from the northwest, one sees significance at once in the present lack of symmetry. The ice sheet, overriding the wall on the northwest side, maintained its cliffs by plucking as on the lee side of a roche moutonnee: but pushing against the wall on the southeast side, it reduced its slope, and, when it melted, scattered over it hundreds of blocks which it was carrying out of the gulf.

There can be no question, it seems to me, in view of the facts outlined above, that these ravines were hollowed out by vigorous valley glaciers before the North American ice sheet came into the White Mountains. If further study should indicate that the block-strewn upper floor of King Ravine, and similar block deposits in the other ravines, are after all true morainic deposits instead of late glacial avalanche and kame deposits, the fact remains that these deposits in question occupy but the upper portions of the cirques; and the post-ice-sheet glaciers of these White Mountains, at best, are scarcely a mile in length.

It will be one of the leading problems in further work in this region to determine whether the cirque-carving glaciers were at work in an early stage of the last glacial epoch, while the ice sheet was advancing towards the White Mountains, or during an earlier glacial epoch. What took place in New England during the Kansan and Illinoian epochs is still in doubt. It seems not improbable that during one of these early glacial epochs, say, the Kansan, the great ice sheet, spreading from the more westerly Keewatin center, and advancing to its outer limit in the middle west, failed to reach New England. Meanwhile local snowfields might have collected on the highest mountains of New Hampshire and Maine, sufficiently large and enduring to nourish glaciers of the Alpine type. The fact that the cirques were probably not occupied at all by local glaciers when the ice sheet last withdrew seems to carry with it the necessity for supposing that cirque glaciers did not develop while the last ice sheet was approaching. There are, however, at least two ways of explaining away this objection. In the first place, the change of climate which brought about the close of the last glacial epoch may have been much faster than the change which earlier introduced the glaciation, allowing too short a time for the local snowfields and glaciers to develop. And in the second place, assuming for simplicity that the oncoming of the cold climate was followed by a return of the warm climate at the same rate, it must be borne in mind that the disappearance of the ice sheet from New England was due to the re-establishment of a climate unfavorable to glaciation, and that by the time the outer margin of the ice sheet had melted back from Long Island, 200 miles to the White Mountains, the climate may have become nearly the same as the climate of to-day. In that case, local glaciers of recent date would be absent. On the other hand, while the establishment of a severe climate with heavy snowfall was causing the ice sheet to spread southward from Labrador towards New England, there must have been plenty of time for local glaciers to grow up on the White Mountains.

The extent of these local glaciers cannot at present be stated. Field investigations on other ranges of the White Mountains, which are contemplated, should throw light on the question. A mass of evidence adduced by Agassiz and Hitchcock to demonstrate local glaciation, particularly in the upper Ammonoosuc valley, must be studied again before their conclusions and those drawn in the present paper are reconciled or proved faulty. The northwestward movement of pebbles and bowlders, reported by Professor Hitchcock,* deserves special scrutiny since upon it rests the main burden of proof that local glaciers extended far and wide through the White Mountains. What little was seen last summer of mountains near the Presidential Range does not encourage the hope that cirques like those near Mount Washington will be found on the other ranges. With this idea the form of the Mount Washington ravines is in full accord. They seem to terminate rather abruptly near the base of the range, instead of finding continuation down the Randolph valley and the Glen. They appear, in short, to represent so many separate cirque glaciers rather than the united tributaries of extensive glacier systems. It is not altogether clear, however, but that the smoother and milder form of these lower trunk valleys may be due to heavy glaciation by the continental ice sheet, which has removed the sharp angles and shoulders from those slopes which were most deeply buried by ice.

Summary.

The peculiar cirque form of certain "ravines" or "gulfs" on the Presidential Range seems accountable only through the former existence in them of local glaciers of the Alpine type. These glaciers, however, appear to have been very short, terminating at or above the foot of the range, within a mile or two of the snowfields, instead of uniting and stretching far down the Ammonoosuc, Connecticut, and other valleys, as earlier investigators have held. The cutting of these cirques must

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*In the Geology of New Hampshire, vol. iii, pp. 239–243, 1878.

have preceded the last advance of the North American ice sheet over the White Mountains, for the bowlder clay of the region extends far up the troughs, nearly if not quite to their heads. Signs of alternation of the side slopes of certain troughs by heavy regional glaciation obliquely across them, likewise, point to an early origin of the cirques. Extensive piles of angular blocks of local rock on the floors of the ravines, at their very heads, resemble deposits in the "basins" of Mount Ktaadn in Maine, which Tarr believed to be valley glacier moraines. If that is indeed their nature, Alpine glaciers existed in these cirques after the ice sheet melted away ; but it is important to note that such glaciers were scarcely half a mile in length and filled less than half the length of the troughs which the earlier glaciers had carved. If, on the contrary, these block piles are not moraines but late glacial or post-glacial avalanche debris, as appears to be the case, they indicate that when the ice sheet last melted away from the White Mountains no local glaciers whatever were re-established. As a working hypothesis it is suggested that the local White Mountain glaciers developed during one of the early epochs of glaciation, possibly the Kansan epoch, and that the last, Wisconsin, epoch was attended by wholesale regional glaciation without local snowfields and valley glaciers.

Dartmouth College, Hanover, N. H.

Art. II.—*An Improved Method of Cleaning Diatoms;* by John M. Blake.

Diatoms are microscopic organisms near the dividing line between animals and plants. It is important for our purpose that they have siliceous skeletons which take on very many symmetrical and beautiful shapes. The chlorophyl and organic matter with which they are associated can be destroyed by strong acids, but they still retain the clay and sand which was deposited with them. The process of cleaning consists in removing this foreign material. Unless this is done the forms will be obscured and difficult to detect.

Many observers have studied and classified the numerous species, and have spent much labor in preparing and mounting them for observation, for there is a fascination in these forms that appeals to all, and any plan for facilitating and lessening the labor of preparation would be likely to induce many more to take up the study.

An ordinary, well-known method of separation is to digest the material with an acid, and then to dilute with water, and allow the heavier portions to deposit. After an interval, the lighter portions are poured away, and the process repeated until the clay, very fine sand and broken diatoms have been removed, while those diatoms which have not been floated away during the process, remain with the coarse sand. This process takes up considerable time, and requires careful attention and timing to decant successfully, and, in spite of this care, some of the smallest and lightest forms can hardly fail to be lost.

The method now to be described was originated by the writer some twenty years ago, and recently, in recurring to the subject, it seemed that even at this date the method might appear novel, since it has not been exhibited during the interval, and no mention of a similar plan has been noticed in any published directions for treating diatoms. Therefore, the way seems open for a revival of interest in the subject, and this method by which, for instance, a small test sample of diatoms can be cleaned in five minutes' time from the acid-prepared material, should appeal to novices as well as experts, by reason of its saving of both time and effort.

The first attempt to supplant the ordinary method of separation and cleaning was made by using a cloth sieve made of partly worn cotton cloth stretched on a frame. The diatom material was treated in the usual way, in a separate vessel with acid. Then, when it had been largely diluted with water, the mass was placed in this cloth-bottomed tray, and agitated and jarred to carry off the clay through the cloth. More water was then added, and the process repeated until only sand and diatoms remained. This plan was not wholly satisfactory, since a large proportion of the diatoms passed through the cloth; yet a considerable bulk of partly cleaned diatoms was obtained, and by careful straining through a sieve the largest diatoms were separated from the smaller and the broken forms, and in this way were secured entirely free from debris. There was an abundance of this material for distribution.

Very soon after this first experiment, the writer originated an improved and more practical method which depended for its success upon the use of cross-sections of wood. Coniferous wood is the most suitable, since it has pores of nearly uniform size, whereas other kinds of wood nearly always have large and small pores commingled, which make them entirely unsuited for the purpose. These wood cross-sections bear dilute acid without injury, which would not be the case with a metal strainer of equally fine mesh, even supposing such a strainer could be made. Furthermore, such a strainer would be too frail to stand the required pressure.

A sharp, thin-edged chisel is used for making the sections, and the wood is kept in boiling water, and removed instantly before each cutting. It requires some care to secure an even thickness, which should be from one-quarter to one millimeter, as needed. The cut section is now to be wetted and surface-dried, and then cemented to a vial, the bottom of which has been cut off for the purpose. A very convenient size can be made from a two-dram vial, making the working aperture of the strainer about one-half inch. The cement may be composed of rosin toughened by wax. Larger strainers may be made, but this size will answer for the first trials.

The digested diatom material, moderately diluted, is to be worked through the wood, a small portion at a time. The acid and the salts will pass with some freedom through this wooden grating, and the clay and fine sand are to be gradually worked out by the alternate pressure and release of a rubber compression bulb. The size used on camera shutters answers very well. This bulb is placed on the end of a glass tube six or seven inches long. It is desirable, but not essential, to have a bulb blown in the middle of this tube. A short bit of rubber tubing of proper diameter is slipped over the free end of the glass tube, and this is to be inserted in the mouth of the vial so as to make a tight joint, but this joint should be easily separable. In operation we take up a small portion of the material in a dropper, and squeezing it into the vial, we insert the rubber tip of the glass tube, and holding the strainer under water, press on the bulb, which will cause the air, acid, and salts to flow out together with a cloud of fine waste material. The pressure is now to be alternately applied and released, and the waste material is thus gradually removed. The discharge of clay and fine sand at last ceases, and the diatoms are left with the coarse sand and mica, which can be removed by other means.

By thus eliminating the clay we will have disposed of one of the most serious obstacles to the cleaning of diatoms. One very important advantage of this method of working is the small quantity of material required because there is very little waste. Successive portions as they are cleared can be united to make up the needed amount.

It is important that the strainer should not be overloaded, for that would cause it to pack and choke. This pack has to be broken up by shaking after each compression, more particularly in cleaning filamentous forms, in order to allow the imprisoned debris to escape at the next compression. As a general rule, and with the more granular forms, this packing requires only a little attention to avoid trouble. Violent compression will fracture many of the larger and more fragile forms of diatoms. The strainer vial should be kept in water when not in use, to avoid injury to the wood-section from contraction.

After the section has been in use for a considerable time the pores gradually become stopped with fine sand. Clay alone does not cause this condition. The only remedy is to cement on a new section.

An interesting point in this connection is that when we burn an old strainer-section for the purpose of studying this clogged condition, we find that the ash will crumble if dampened, and will fall into numerous "sticks," each the length and diameter of a pore of the wood, and each of these "sticks" will be found to be packed with the small sand grains.

It may be said in regard to the selection of wood, that white pine—*Pinus strobus*—is excellent for ordinary use, since the strainers cut therefrom work freely, Certain light diatoms that would as a rule have been floated away in the usual settling and pouring-off process, are here retained by the pine section, because their length enables them to bridge across the pores. Some very short forms, however, will pass through to a considerable extent.

By saving the tailings from the pine and passing them through a spruce strainer, the majority of these short forms were retained. The spruce here referred to was a piece of flooring, and of a very white species of spruce. It was not identified. There are several other species that would probably answer equally well. In using spruce, the sections should be thin. The clay will be found to pass through the pores of spruce with some freedom, but not so rapidly as through pine.

There are some gatherings that will require a strainer of still finer grain. This may be said of the very smallest diatoms that grow on water plants. The majority of these may be retained by a quite thin section cut from the white outer wood of the red cedar *Juniperus Virginiana.* In one experiment some of these very minute forms which had passed through the spruce were almost wholly retained by the red cedar.

It follows that from these three species of wood we can obtain a graded series of strainers, each capable of separating the clay from the diatoms, and at the same time furnishing a ready means of grading as regards size.

The pine strainer works the most rapidly and makes a very good separation, and will meet ordinary requirements. The spruce strainer can follow if we want a more thorough gleaning of the smaller forms; and then we have the red cedar section as a final resort to aid in securing the very smallest diatoms.

Art. III.—*A new Occurrence of Silver, Copper, and Cobalt Minerals in Mexico;* by Frank R. Van Horn.

Introduction.

The minerals which are the subject of this paper were found at the Veta Rica mine, Sierra Mojada, Coahuila, Mexico. The specimens were presented to the Case School of Applied Science by Mr. R. B. Cochran, who was at the time superintendent of the Compania Metallurgica Mexicana at the mine mentioned. Our thanks are due Mr. Cochran for some very interesting as well as valuable specimens. The Sierra Mojada is a mining region in the extreme western part of the state of Coahuila, about 494 miles south of El Paso, Texas. It is reached by the Mexican Central and Mexican Northern railroads via Escalon. The district was a silver-lead camp up to 1893, and is still so, although since that date large amounts of silver-copper ores have been found.

Although ore has been mined during most of the period since it was discovered in 1878, very little has been published about the locality. Up to 1911, as far as the writer is aware, there have appeared but two articles, which were written in 1886 by Chism,[*] and in 1901 by Malcolmson.[†] Both of these papers cover the mining and metallurgical methods employed in the region, and little, if any, attention has been paid to the mineralogy, although the geology has been briefly considered. In 1911, a new occurrence of the rare mineral pearceite was described from this locality.[‡] The last and most recent article[§] on the district appeared in 1912, and discusses the geology and economic geology in the light of more recent developments. Since, therefore, the previous literature on the region is not of a mineralogical nature, it has seemed to the writer that it might be fitting to discuss rather briefly the mineralogy of the district.

The ore minerals are found at or near the contact of a Cretaceous limestone with what has been called a "porphyritic breccia," although it much resembles a decomposed rhyolite, or rhyolite tuff. Full details about such features, as well as

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[*] Sierra Mojada, Mexico, by Richard E. Chism, Trans. Amer. Inst. of Min. Eng., xv, 542, 1886.

[†] The Sierra Mojada, Coahuila, Mexico, and its Ore Deposits, by James W. Malcolmson, Trans. Amer. Inst. Mining Eng., xxxii, 100, 1901.

[‡] A New Occurrence of Pearceite, by Frank R. Van Horn and C. W. Cook, this Journal, xxxi, 518, 1911.

[§] The Occurrence of Silver- Copper- and Lead Ores at the Veta Rica Mine, Sierra Mojada, Coahuila, Mexico, by Frank R. Van Horn, Bull. 68, Trans. Amer. Inst. Mining Eng., p. 867, August, 1912.

the mines of the region, may be found in the papers previously cited.

Minerals Occurring at Veta Rica Mine and Elsewhere in the District.

The writer has been able to identify 21 different minerals in the ores and veinstones of the Veta Rica mine. These are grouped according to the arrangement of Dana's System of Mineralogy as follows:

Native Elements—Sulphur, silver, copper.
Sulphides—Argentite, galena, chalcocite, covellite, chalcopyrite.
Sulpho-salts—Proustite, pearceite.
Haloids—Cerargyrite var. embolite.
Oxides—Cuprite, hematite, limonite.
Carbonates—Calcite, cerussite, malachite, azurite.
Arsenates—Erythrite.
Sulphates—Barite, gypsum.

In addition to these, Mr. Cochran in a personal communication vouches for the presence of sphalerite in small amounts. Chism* mentions in the district among others, pyrolusite, psilomelane, quartz, silver chloride, and lead sulphate; and Malcolmson† speaks of the presence of "copper oxide," and "zinc carbonate." In all, it would seem that 28 minerals have been identified from Sierra Mojada up to the present time. Of these, eight have never been mentioned by any one except the present author, and, therefore, may certainly be claimed as new occurrences. These minerals are as follows: copper, calcite, malachite, chalcocite, covellite, proustite, pearceite, and erythrite. There is also some uncertainty as to whether embolite and cuprite have been previously recognized, although Chism speaks of the presence of silver bromide in small amounts, and Malcolmson mentions copper oxide without further specifying whether it is cuprite or tenorite.

Description of Minerals found at Veta Rica Mine.

Because of the fact that nothing has been observed in mineralogies concerning Sierra Mojada, it has seemed advisable to give a short description of the occurrence of the minerals from the Veta Rica mine which have been determined by the writer. One interesting feature of the specimens is the almost universal presence of gypsum as a gangue mineral. Barite is nearly as common, whereas quartz was not identified, and calcite was found in but few places.

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* Op. cit., page 550.

† Op. cit., pages 107 and 131.

Sulphur.—This mineral is found massive in considerable quantities in the upper levels, and has been exploited for market in other mines of the region. It is often very pure, but in some places is mixed with gypsum, cerussite, and limonite. Chism ascribes the formation of the sulphur to heat, but it was more probably formed by the normal oxidation of sulphide ores, due to the action of hydrogen sulphide on limestone or sulphur dioxide, or by the reduction of gypsum which is so generally present.

Silver.—Silver is found massive, in wires, plates, and irregular globular forms. It has been found in three different associations: as grains and wires with argentite in barite; with embolite in the siliceous limestone ores; and in hair-like masses, and globular incrustations on erythrite in barite.

Fig. 1.

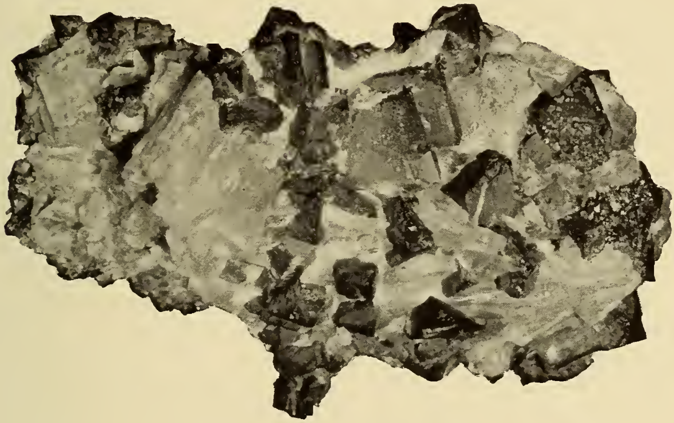

Fig. 1. Cubes of Copper in matrix of Selenite from the Veta Rica mine.

Copper.—This is present as perfect cubes which have a varying diameter up to five-eighths of an inch. The edges are in some places slightly modified by a tetrahexahedron. It is rare to find such undistorted crystals of native copper. The crystals are partially coated with cuprite, and are embedded in a matrix of white cleavable gypsum. This is an association which the writer has never seen, although copper is said by Dr. E. O. Hovey, of the American Museum of Natural History, New York City, in a personal communication, to be found with gypsum at Painesdale, Michigan. A photograph of the Veta Rica occurrence is shown in fig. 1.

Argentite.—This mineral occurs massive, and also in irregular rounded forms. On two specimens it was present in distorted crystals of octahedral habit. It is associated in one place with proustite, and in another with silver and barite. One specimen shows many four sided pyramids (evidently octahedrons) each attached to the extremity of wires of silver. It is certain that one mineral originated from the other, but it is impossible to tell which is secondary. An analysis of the argentite was made by Dr. N. A. Dubois, formerly of the Chemical Department of Case School of Applied Science, with the following results:

	Found	Theoretical
Ag	86·18	87·07
S	13·18	12·93
Cu	0·70	0·00
	100·06	100·00
Sp. gr.	7·40	7·2–7·4

The specific gravity given was obtained from the average of six determinations made on two different specimens by means of Jolly balance and pyknometer. The most interesting fact indicated by the analysis is the presence of an appreciable amount of copper. This shows a gradation toward the mineral jalpaite $(Ag,Cu)_2S$, which has been found at but one or two places in the world. It will be shown later that the proustite with which it is associated also contains about the same amount of copper.

Galena.—This mineral is found in fine granular to somewhat fibrous masses. Specimens are occasionally coated with cerussite as a decomposition product, but no anglesite was observed.

Chalcocite.—This is present in very pure large compact masses showing conchoidal fracture. It is found in some places with chalcopyrite and barite.

Covellite.—Covellite occurs in very dense fine-grained masses which with the exception of color have the external appearance of chalcocite. On a fresh fracture, the mass is shown to consist of small indigo blue grains which possess the basal cleavage of covellite. Possibly the mineral has resulted from the alteration of chalcocite, on which it is commonly found as a tarnish.

Chalcopyrite.—This is found in compact masses alone, or mixed with chalcocite.

Proustite.—The mineral is present in compact masses of brilliant ruby-red color. It shows a distinct rhombohedral cleavage. On one specimen it occurs with argentite, whereas in another place it is associated with calcite in seams of gray magnesian limestone. The mineral was analyzed by Dr. N. A. Dubois with the appended result:

	Found	Theoretical
Ag	64·65	65·40
Cu	0·70	----
S	20·18	19·43
As	15·25	15·17
Sb	Trace	----
	100·78	100·00
Sp. gr.	5·60	5·57–5·64

The specific gravity was obtained by taking the average of six determinations on three pieces, using both pyknometer and Jolly balance. The analysis shows that the pure proustite molecule is present, since but a trace of antimony was found. A small amount of copper, which was also obtained in the argentite, is present. This is quite unusual for proustite, but when one considers that both argentite and proustite are more or less associated in the same ore body with pearceite, $(Ag,Cu)_{16}As_2S_{11}$, one need not be surprised if they contain copper, since copper-silver solutions were evidently prominent in the deposition of ores at this particular place.

Pearceite.—This very rare mineral was fully described* in this Journal in 1911. It might, nevertheless, be mentioned that the analysis of the mineral caused the conclusion that a more logical formula for it might be $(Ag,Cu)_{16}As_2S_{11}$, rather than $(Ag,Cu)_{18}As_2S_{12}$ which was originally proposed. In accordance with these facts, the formula of the isomorphous polybasite should be $(Ag,Cu)_{16}Sb_2S_{11}$, rather than $(Ag,Cu)_{18}Sb_2S_{12}$ which was proposed by Heinrich Rose in 1829.†

Cerargyrite var. Embolite.—In recent investigations by Prior and Spencer‡ they suggest that cerargyrite be employed as a group name, and that embolite should be regarded as a sub-species of the group. The mineral occurs in well-defined cubo-octahedral crystals on cracks and in pores of an iron-stained limestone which is siliceous in places if judged by analyses, although no quartz could be recognized even in thin sections. This limestone is brecciated locally, and the embolite is also found as irregular concretionary coatings on the brecciated surfaces. Consequently the embolite is an impregnation of the breccia, and not a replacement of the limestone. Thin sections show the mineral to occur only in the cracks. Both crystals and coatings have a bright sulphur-yellow color, and possess a resinous to adamantine luster. It is associated

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* Op. cit.

† A Discussion of the Formulas of Pearceite and Polybasite, by Frank R. Van Horn, this Journal, xxxii, 40, 1911.

‡ Min. Mag., xiii, 174.

with silver in some places. The mineral was examined both by the wet method and the blowpipe, and distinct tests for bromine were obtained, although chlorine is certainly largely in excess. Nevertheless, the combined evidence of the chemical tests and the bright yellow color lead to the conclusion that the mineral should properly be called embolite. The writer was able to discover several spinel twins, which as far as is known have not been previously recognized on this species. With great care several crystals were detached from the limestone matrix. These were measured on a two-circle Goldschmidt goniometer, and drawn by my friend, Professor Victor Goldschmidt of Heidelberg University, Germany, and I wish to thank him for his kindly assistance in this matter. A top view of one such crystal is shown in fig. 2, and a side view of the same crystal is seen in fig. 3. In addition to the twinning after the spinel law, the following forms were observed:

Fig. 2.

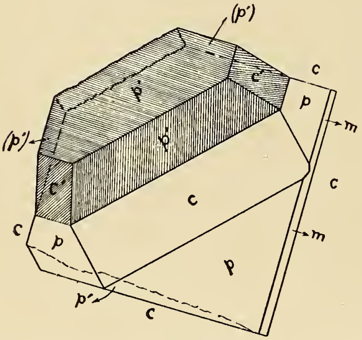
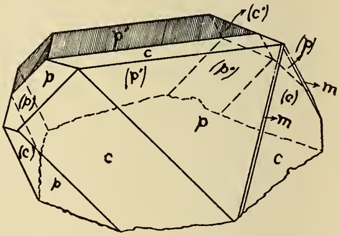


Fig. 3.



Figs. 2 and 3. Spinel twin of Embolite, Veta Rica Mine. Fig. 2 is top view, and fig. 3 is a side view.

Letter designation of face	Goldschmidt	Miller	Naumann	Dana
c	0	(001)	∞ O ∞	*i*–*i*
p	1	(111)	O	1
m	$\frac{1}{3}$	(311)	3O3	3–3

The cube and octahedron are found in about equal development. The form *m*, which is found in but two faces, is that of an icositetrahedron (311,3–3) which has not been previously observed on any minerals of the cerargyrite group as far as the writer is aware. Consequently that form, as well as the twinning, seems to be new for embolite.

Cuprite.—This is found mostly massive granular, associated with malachite, azurite, and gypsum. It is also present in brilliant ruby red crystals on the copper cubes shown in fig. 1. These crystals are very small and could be recognized only as cubes modified by at least two other forms.

Hematite.—It occurs chiefly as earthy masses in the limestone. It is found in botryoidal and stalactitic forms at the Esmeralda mine in the same district.

Limonite.—This mineral has the same occurrence as hematite, both in the Veta Rica and Esmeralda mines.

Calcite.—As has been stated previously, calcite does not seem to be common as a gangue mineral in this locality. It was found in one place as small doubly terminated scalenohedral crystals in drusy cavities with argentite and silver. On another specimen, it was seen in granular masses with proustite in seams in limestone.

Cerussite.—Cerussite occurs in granular, almost friable, masses, in large quantities in the upper levels, where it is associated with gypsum and sulphur. It was the original ore of the camp, and is still important. It always contains silver values in paying quantity. Cerussite was also seen as a coating on galena.

Malachite.—This mineral is found in small acicular crystal aggregates and coatings with azurite, cuprite, and gypsum.

Azurite.—Azurite is present in tabular crystal aggregates, and has the same association as malachite.

Erythrite.—This mineral is found rarely in single crystals, but generally occurs in stellate and rosette-like crystal aggregates which have a beautiful peach pink to nearly crimson color. The earthy varieties so common at Cobalt, Ontario, and elsewhere were not observed. The crystals are all distinctly tabular after the large clinopinacoid (010), which habit has not been previously observed. Other forms noticed were a prism, a positive pyramid, a negative orthodome, and probably also the orthopinacoid (100), all of which were small. The two terminal forms are somewhat rough, and the dome face is always larger than the pyramid. With the exception of the pronounced tabular habit, the crystals resemble the drawing made by Green.* The crystals were striated vertically, aud the cleavage after the clinopinacoid was perfect. The luster on the cleavage face was pearly, and elsewhere was vitreous. The mineral occurs in little veins and cavities in barite, and is also associated with silver. In all places, however, the silver rested upon the erythrite, and, therefore, was deposited later. No cobalt arsenides or other cobalt minerals have ever been observed from

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*Crystallization of Erythrite from Cobalt, by W. F. Green, Trans. of the Canadian Institute, viii, 443, 1908-9.

the region, but it seems certain that such must exist, and that the erythrite has resulted from their decomposition.

Barite.—Barite is common as a gangue mineral in granular and lamellar crystalline aggregates. In thin sections, plumose aggregates were observed which were associated with argentite and silver.

Gypsum.—This substance seems to be present nearly everywhere as a gangue mineral. It has always a tabular to scaly habit, and consequently much resembles muscovite, which, however, never occurs at this locality. It is often white, but in places is stained red by iron oxide. Crystal faces are present in places, but are generally rough or curved. It is possible that the original mineral may have been anhydrite, which has been shown by Lindgren* to be a gangue mineral in some localities. However, in this district it is probable that the gypsum was directly precipitated by the interaction of solutions containing metallic sulphates and carbonates.

In regard to the other minerals mentioned by Chism† such as pyrolusite, psilomelane, quartz, silver chloride, and lead sulphate, they were not present on the specimens investigated by the writer. Neither was the zinc carbonate spoken of by Malcolmson.‡ However, there is little doubt that they are to be found in the district. In any event there are but seven minerals ever mentioned as having occurred in the camp which the writer has not seen in well-defined specimens. Any other species which are not included in the above list of 28 mineral will have to be regarded as an addition to the mineral species found in the Sierra Mojada district as far as has been observable from existing literature.

Geological-Mineralogical Laboratory,
Case School of Applied Science.
Cleveland, Ohio, September, 1912.

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*W. Lindgren: Anhydrite as a Gangue Mineral, Econ. Geol., vol. v, No. 6, p. 522, 1910.

† Op. cit.

‡ Op. cit.

ART. IV.—*Vertebrate Footprints in the Lower Permian of Kansas*; by ROY L. MOODIE.

AMONG other objects of interest in Baker University Museum at Baldwin, Kansas, of which may be mentioned a Silurian starfish belonging to the modern order Phanerozonia, and a Dakota Cretaceous turtle, there are some slabs of soft lime rock or gypsum which contain a series of very interesting footprints. Footprints are so rare in the Permian of Kansas that every occurrence is to be regarded with interest. The present footprints, if properly interpreted, will prove of unusual interest to paleontologists on account of the lack of knowledge of the group of animals which these footprints seem to indicate. There are several possibilities for the footprints, the theropod dinosaurs, the parasuchians or amphibians.

The single footprint here figured was accompanied in the quarry by many others and it is hoped that an exploration of the deposit may reveal other objects of interest. The quarry lies two miles northwest of Eureka, Greenwood County, Kansas, and was discovered in 1902 by Dr. C. S. Parmenter of Baker University, to whom I owe the privilege of describing these interesting relics. The exploration was carried on under difficulties since the owner of the land was highly suspicious of the value of the slabs containing the footprints, which, consequently, had to be secured under cover of darkness, and thus rendered intelligent exploration impossible. The deposit, Dr. Parmenter tells me, is a thin uniform layer of soft, white rock in the flint hills, which, according to the explorations of the Kansas Geological Survey, occur on the line between the Upper Pennsylvanian and Lower Permian.

There are two slabs containing the impressions, one of them exhibiting two footprints which seem to be of the same series. The slab figured also shows impressions of some of the animals' activities, but just what I cannot determine. The impressions are firmly, and save for subsequent erosion which has obscured them somewhat, sharply defined in the soft rock, which formed the mud on the shore of the bayou or lake in Permian times, and along which the animal walked, leaving only his footprints. It is to be regretted that the skeletal elements of this Permian vertebrate are still lacking, but it is to be confidently expected that future explorations will reveal something of the nature of the animal which made these footprints.

The nature of the foot impression corresponds very closely with that of an undoubted theropod dinosaur, but to say that the impression is a dinosaur footprint is further than the writer cares to go. If it is a dinosaur it would seem to indicate that the group arose in Carboniferous times. The three-toed condition of the footprint, the elongate backward extension of the heel all agree with the impressions the theropod dinosaurs left in the Triassic sandstones of the Connecticut Valley. That the impression was made by an amphibian of some kind is possible, but we know at the present time no three-toed member of that group. No parasuchian is known with an elongate heel and none with only three toes such as the impression indicates. That the impression was made by a bird is much more out of the question. At the time when these footprints were made we know of several groups of air-breathing vertebrates in other portions of this continent and elsewhere. Aside from the amphibians there were the theromorph reptiles which agreed very closely with the higher Amphibia in foot structure.

It will thus be seen that while the exact nature of the impression is uncertain, no one can deny that it is a footprint nor can it be denied that the impressions exhibit characters which are those of the theropod dinosaurs. Future discoveries may result in a further explanation of the nature of these interesting impressions; but again, this may remain as has *Eosaurus*, *Thinopus antiquus* and other discoveries, the only evidence we have of the existence, in the closing period of

Paleozoic times, of a group of animals which were abundant and highly developed in later geological time.

Measurements of the footprints.

Small footprint.

Length of middle toe and heel impression	135^{mm}
Length of side toe	65
Width of heel impression	18
Width of impression of middle toe	11

Larger footprint with portion of heel impression eroded.

Length of middle toe and heel impression as preserved	135^{mm}
Estimated length	170
Length of side toe impression	90
Width of heel impression	20
Width of toe impression	15

University of Kansas, Lawrence, Kansas.

Art. V.—*The Dinosaurs of East Africa;* by Charles Schuchert.*

Since the discovery of Gigantosaurus by Professor Fraas in 1907 in German East Africa, all paleontologists and especially Americans have been closely following the work of the expedition sent out by the Geologic-Paleontologic Institute of the University of Berlin under the direction of Professor Branca. In his beautifully illustrated book Doctor Hennig tells us in an interesting way how the expedition lived, what it did, and all about the country where the work was done, its people, and the rest of its organic world.

It was Engineer B. Sattler, stationed at Lindi, who made the original discovery of the dinosaur remains in the hills of the Tendaguru district and who informed Professor Fraas of them while the latter was in East Africa in 1907. When this great discovery was reported by Professor Fraas to his countrymen, the further securing of material for Germany was not only regarded as desirable but became a national pride and necessity. A committee was formed by Professor Branca and under the protectorate of His Highness, Herzog Johann Albrecht of Mecklenburg, a call for financial help was sent out, and this was quickly responded to by individuals and corporations.

The expedition left Marseilles on the thirteenth of March, 1909, under the leadership of Doctor W. Janensch, assisted by Doctor Edward Hennig, both of the University and the Natural History Museum of Berlin. They arrived in the Tendaguru region of German East Africa on the sixteenth of April, toward the end of the rainy season, and remained at work for two years and six months, and then returned home, but the digging still goes on under other field operators. During the first three years about $45,000 was expended by the expedition, resulting in some 4,000 packages of bones and other natural history material. These packages in general weighed about 60 pounds each, but there were many heavier ones requiring anywhere from two to twenty-five men to carry them across the country—a march of about five days along the native trails—to the sea shore. Plaster had to be obtained from Berlin and lumber for boxes from Norway. Recently the Prussian Government voted $12,500 for the field season of 1912.

The men of the expedition adapted themselves to the tropical climate and educated the negroes to dig out the bones and to

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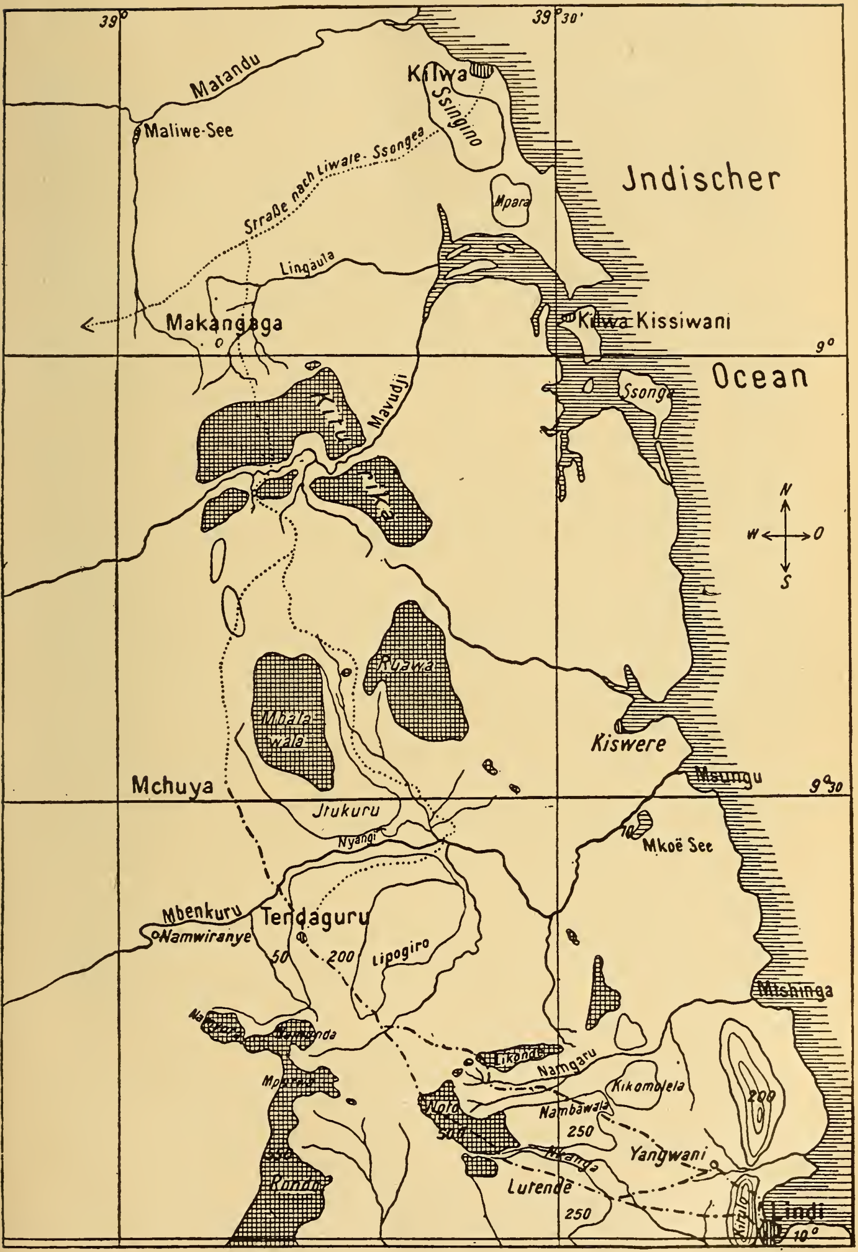
* *Am Tendaguru. Leben und Wirken einer deutschen Forschungs-Expedition zum Ausgrabung vorweltlicher Riesensaurier in Deutsch-Ostafrika,* von Dr. Edw. Hennig, Stuttgart, 1912, 151 pages, 1 map, 62 figs. and 9 plates.



Map of the Dinosaur localities of German East Africa.

harden and pack them; many porters had to be secured to carry the packages to the port, Lindi, where the bones were boxed and sent to Berlin. It was a great undertaking in the midst of malarial fevers, under very strange conditions, and in a more or less tropical wilderness. At first they had 150 negroes, but later they employed nearly 500; throughout the second working season they always had as many as 400.

The hill Tendaguru, less than 100 feet high, lies isolated on a high, thickly wooded plateau averaging about 650 feet above the sea, and is the central point from which all of the diggings have been operated. It is in the midst of an extensive dinosaur cemetery, for at one time there were twenty exhumations in operation scattered over 30 square kilometers, or across one degree of latitude (between 9° and 10° S. and 39° and 39°30′ E.). The localities are shown on the accompanying map.

In a thickness of about 500 feet exposed along the stream Mbenkuru are found three distinct horizons of soft shale with dinosaur remains, separated from one another by hard coarse-grained sandstones to conglomerates that have an abundant marine invertebrate fauna. Each marine division has its own assemblage of forms, and makes terraces along the river valley. While the marine fossils have not yet been determined, still Doctor Hennig states that the time represented is not of the higher Cretaceous as was first supposed but of earliest or lowest Cretaceous age, comparable to the earlier dinosaur horizon of America, *i. e.*, Morrison or early Comanchian (p. 48). All of the beds are of one continuous series of deposits, as the different horizons grade into one another. The conditions of deposition therefore appear to have been an alternation of exceedingly shallow marginal seas that came to be filled with detritus and changed into great mud flats flooded by rivers and possibly in part by high tides. Three such cycles are recorded. Dinosaur bones do not occur in the marine deposits but begin in the transition zones, where they occur with Belemnite guards, and may be so abundant as to make bone conglomerates. Where the bones occur in greater abundance there appear to be no marine invertebrates.

In the lowest dinosaur zone there is but little good material, while the highest one is not at all so rich in remains as is the middle division, out of which most of the bones and fossil woods have been taken. One quarry was worked by many negro laborers throughout the dry seasons of two years, so rich in dinosaur remains are some of the places. In each of two quarries at least fifty small individuals were huddled together, not one of which retained a skull. At the base of the middle dinosaur horizon is found a bone conglomerate made up of the larger and thicker bones, mainly those of the limbs, all of which are much broken and water worn. However, parts of many individuals do occur singly, but the bones usually lie all in a jumble. Very rarely do the skeletons occur undisturbed and connected, and no complete single skeleton has as yet been found after three years of work. Most of the isolated skeletons consist of leg bones, a foot, part of a vertebral column, a shoulder blade, and so on. Some of the bones also show teeth marks of carnivorous dinosaurs or other flesh-eaters. From these it appears that the skeletons have been torn apart by carnivorous animals and by the action of running water.

Skulls are exceedingly rare and only two fair ones were secured, but dismembered parts pertaining to the largest dinosaurs are not so rare. Teeth are common and in fine preservation and great variety.

It is the ambition of the Berlin Museum to set up at least one skeleton of Gigantosaurus and parts of as many others as are necessary to show the variety, size, and structure of the East African dinosaur assemblage. The largest African animals of that time were truly gigantic in size, exceeding by far the mightiest of American Comanchian dinosaurs. It is thought that the largest attained almost twice the length of Diplodocus, which is 80 feet long. The neck appears to have been at least 15 feet longer than that of Diplodocus and a good deal thicker, as the vertebræ of Gigantosaurus are nearly twice as high as in the American genus. Truly they were the "largest of all known land animals" and "it is very difficult to picture to ourselves the enormous size of such living masses" (51).

Doctor Hennig speculates much as to how these animals came to be entrapped and buried in the sediments. The following is suggested by him as the most plausible explanation :

"We can accordingly assume that a very shallow sea flooded vast areas of marsh land, and at times of ebb the dinosaurs wandered far out over these flats to feed on algæ, sea-weed and small marine animals, only to be caught in low places by the incoming tides and so drowned and eventually buried. In some cases feet were found standing upright, leading to the conclusion that the animal had become mired in the mud. Because of the very small size of the brain, we may ascribe to them a low mentality and consequently frequent recurrences of the accidental drownings. We may also assume that the flesh-eating animals of the water as well as of the land fed on these cadavers. This explanation, of course, does not readily apply to the gigantic forms since they could easily have waded out of the flooding waters, but they may have lost their sense of shore direction and, becoming confused, gone into the deeper waters and drowned. We may also assume, since the strand line repeatedly rose and fell, as is indicated by the changing character of the strata, that large land masses were separated into islands and that these were finally submerged beneath the sea with all the life upon them" (57–9).

In conclusion:

"We may picture to ourselves as follows the wonderfully varied life that dwelt along the strand of this Cretaceous sea. Here trod those dull-witted giants whose necks were more than 12 meters long and up to 2 meters thick, with length of legs exceeding any known size; here hurried about the dragon-tribe, large and small, down to the tiniest lizard; here appeared herds of armored dinosaurs, terrible in shape, with mighty spines along the back and tail; here hastened past small swift saurians erect upon their hind legs, while others flew through the air; here were the fearsome flesh-feeding robbers and the Gigantosaurians who alone because of their size could escape living from them and who fed their huge bodies upon plants and smaller sea animals. Scarcely can the noble and prolific animal life of Africa today compare in diversity with that assemblage which here lies before us" (59).

ART. VI.—*The Recombination of Ions Produced by Röntgen Rays*; by S. J. PLIMPTON, Ph.D.

WHEN a gas is exposed to the continued action of Röntgen rays the number of ions contained in a unit volume of the gas does not go on increasing indefinitely because of the electrostatic field associated with the ions. A continuous diffusion takes place from the region of maximum ionization and in addition oppositely charged ions recombine under their attractive forces. The process of diffusion is a relatively slow one, and with properly designed apparatus, may be disregarded in measuring the changes in ionization due to recombination.

According to the accepted theory of ionization in gases the rate of change of the number of ions of either sign per unit volume is proportional to the square of this number, i. e.

$$\frac{dn}{dt} = -an^2 \qquad (1)$$

where a is a constant known as the coefficient of recombination and is independent of n.

This law of recombination has been shown by several experimenters to hold good to a high degree of approximation.

In the early experiments of Rutherford* and of McClung† the gas was confined in a closed metal chamber provided with an aluminium window for admitting the rays. Inside the vessel were two parallel metal plates, one of which was connected with a source of potential and the other with an electrometer system. Under the action of the rays the gas between the electrodes was ionized until a steady state was attained when the ionization was balanced by diffusion and recombination; the rays were then switched off and the charge remaining in the gas at definite times after the cessation of the rays was then determined. A pendulum interrupter was provided so that this time interval could be varied at will. In this manner corresponding values of n and t were obtained and were found to agree satisfactorily with the relation

$$\frac{1}{n} - \frac{1}{n_0} = at \qquad (2)$$

which is obtained immediately by integrating equation (1), n_0 being the number of ions per cubic centimeter present in the gas when the steady state has been established, and n being the corresponding number after the ions have been allowed to recombine for a time t.

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* Rutherford, Phil. Mag., xliv, p. 422, 1897.

† McClung, Phil. Mag., xiii, p. 283, 1902.

Another method was also employed by McClung* to demonstrate the validity of the law of recombination and was used by him to determine an absolute value of the coefficient a. The saturation current was measured while the rays were acting, a strong electric field being maintained across the electrodes. From this observation the number of ions (q) produced per cubic centimeter per second in the gas was determined in arbitrary units. The electric field was then withdrawn and the rays were allowed to act until a steady state of ionization was produced; this is represented by the equation

$$q = an^2 \tag{3}$$

where n denotes the number of ions of either sign present per cubic centimeter in the gas when the steady state has been reached. The rays were then cut off and a strong electric field immediately applied sufficient to drive over to the electrodes all the ions remaining in the gas. By measuring the charge given to the electrodes n was determined. The determination of both q and n sufficed to afford an absolute estimation of a.

Rutherford† and Townsend‡ made use of another method for verifying the law of recombination. The saturation currents were measured at different parts of a tube through which ionized air was streaming. These currents give the values of n at the place of observation, and if the rate of flow of the air is determined and the distance from the region where the ions are formed is known, the series of values of n corresponding to different time intervals can be plotted. This method can be employed only when the gas used is available in large quantities.

Langevin§ has shown that the coefficient of recombination a is capable of being expressed in the following form

$$\frac{a}{e} = 4\pi(k_1 + k_2)\epsilon$$

where e denotes the charge on the ions, k_1 and k_2 the ionic mobilities, i. e. the velocities with which the positive and negative ions respectively move under unit electrostatic field, and ϵ is a number which is less than unity. According to the theory of Langevin, e represents the ratio of the number of collisions between oppositely charged ions which result in recombination to the total number of collisions; in this theory it is assumed that the ions move under their mutual attractions following the same law and with the same mobilities as if they moved

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* Loc. cit. † Loc. cit.

‡ Townsend, Phil. Trans., A, p. 157, 1899.

§ Langevin, Ann. Chim. Phys., xxviii, p. 289, 1903.

under the influence of an externally impressed field. The following method was devised by Langevin for the experimental determination of e. The gas between the two parallel-plate electrodes was ionized by a single flash of very short duration from a Röntgen ray bulb; the ions are regarded as being formed uniformly in layers parallel to the electrodes although the density of ionization may vary from one layer to another. The charge communicated to the electrodes for electric fields of different intensity is measured by an electrometer; the electric field between the plates is in general chosen very small so that appreciable recombination may take place during the passage of the ions through the gas. The charge Q brought over by a field X is given by the formula

$$Q = \frac{X}{4\pi\epsilon} \log \left(1 + \frac{4\pi Q_0 \epsilon}{X}\right)$$

where Q_0 is the charge corresponding to a field of sufficient intensity to prevent appreciable recombination.

Applying this method and making use of the previously determined values of k_1 and k_2, Langevin found that the values of a showed a considerable falling off when the air pressure was reduced below one atmosphere, whereas the experimental results obtained by McClung,* who used the method described above, had assigned a value to a which was practically independent of the pressure below one atmosphere. This discrepancy was almost certainly due to the abnormally large corpuscular radiation which proceeded from the electrodes in McClung's experiment when the Röntgen rays were acting.

It is convenient to indicate here briefly three main sources of error which are liable to occur in the course of experimental work on this subject.

(1) Diffusion of the ions.

(2) Presence of corpuscular radiation proceeding from the electrodes.

This gives an abnormally high density of ionization near the plates, making the value of a greater than for a uniform distribution. The error becomes greater as the pressure is reduced.

(3) Variations in the intensity and penetration of the Röntgen rays due to continued working of the bulb.

The method adopted in the present series of experiments reduces these sources of error to a minimum. It consists essentially in ionizing the gas between two parallel-plate electrodes as uniformly as possible by means of a single flash from a Röntgen ray bulb, allowing the ions thus produced to

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* Loc. cit.

recombine in the absence of any external field for small intervals of time which can be regulated and determined mechanically, and by the sudden application of a strong electric field driving over to the electrodes those ions which remain in the gas. In this way we obtain a series of values of n corresponding to different values of t, and values of a are then determined for different conditions of gas pressure by means of a variation of equation (2) which is indicated below.

This method is believed to have the following advantages:

(1) By using radiation of smaller intensity and by shortening the time intervals, the effect of diffusion is greatly reduced.

(2) By restricting the beam of rays between the electrodes, diffusion is further reduced and corpuscular radiation practically removed.

(3) By the use of single flashes of X-rays the difficulty of maintaining uniformity in the rays is greatly lessened.

(4) Since the duration of the flash is very brief, it is possible to study the initial stages of recombination.

In connection with (4) it is worthy of mention that in previous investigations, no information has been afforded with regard to the initial stages of recombination. In a steady state of ionization, ions of practically all ages are present, diffusion has become very appreciable except in the case of the ions of recent formation and the ionization is necessarily very intense, so that on the whole, a practically uniform distribution of the ions prevails at the instant when the rays are cut off.

With single flashes of Röntgen rays the case is different. At the instant when the flash has ceased the ions are approximately all of the same age and diffusion has been practically inoperative so that any peculiarity in the initial distribution of the ions is capable of being detected by experimental observation. Such an initial effect has made itself manifest in the present series of experiments and will be described later.

Preparation of Gases and Vapors.

The carbon dioxide gas used in these experiments was obtained in the usual way by the action of hydrochloric acid on marble in a Kipp generator. The sulphur dioxide was taken from a cylinder of the compressed gas. The vapors were evaporated in each case from the liquids as supplied by the chemist. In all cases before admitting the gas or vapor, the apparatus was pumped out to a few millimeters of mercury. The substance to be tested was then let in until the greatest allowable pressure was reached and again pumped out as before. This process was repeated at least three times.

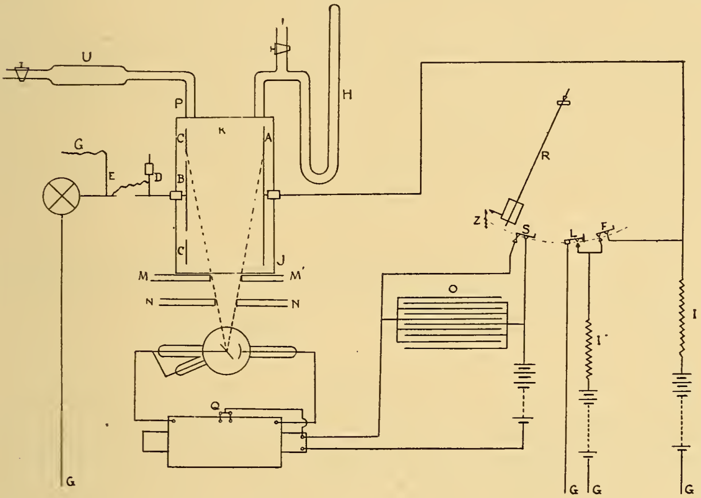
Great care was taken in every case to make the gas or vapor dust free by passing it through several inches of glass wool and then allowing it to settle for several hours.

The gases were dried by passing slowly through a tube containing phosphorus pentoxide and the vapors were bubbled through sulphuric acid when necessary and were always passed through a calcium chloride drying tube.

Description of Apparatus.

The general arrangement of apparatus is shown in fig. 1. The ionization chamber K is lined with aluminium and provided with two parallel plate electrodes A and B of aluminium, the latter being surrounded by a guard ring C which is connected with the walls of the chamber. The insulated electrode B may be connected with an electrometer by means of a key D. The beam of X-rays is restricted by adjustable lead screens MM′ and NN′ so that it does not fall on the electrodes. A pendulum R is used for automatically giving the flash of X-rays by opening the key S and, after a definite interval of time, applying a potential to the electrode A by opening the switch F, which may be placed at any position along the path of the pendulum.

Fig. 1.



In order to obtain X-ray flashes of sufficient intensity it was sometimes necessary to interrupt a current of 25 amperes at the key S. Although a large adjustable condenser was used for suppressing the spark, considerable difficulty was experienced at first in getting uniform conditions in the induction coil at the instant when the break occurred in the primary circuit. This difficulty was overcome by the use of a specially constructed key for breaking the large primary current.

In designing keys for purposes of this sort, attention has usually been centered on getting a rapid motion at the instant of break. It was found possible to use very moderate motion provided a firm uniform pressure was maintained between the contacts up to the instant of breaking and separation of the contacts then effected without vibration or chattering. The most successful break was constructed as follows:

A rigid bar armature of T section was mounted in conical bearings at one end and carried a platinum contact at the other. The complementary platinum contact was mounted rigidly on the same heavy base with the bearing. The key was closed firmly by a permanent horse-shoe magnet. The bearings were kept in such adjustment that the magnet could just overcome the friction at a particular position. The bearing screws were locked in place by another pair of set screws. A looseness in these bearings, which was not sensible to the touch, would vary the electrometer readings from five to ten per cent.

When this key was used with a current strong enough to properly excite the bulb, the flashes of X-rays produced almost perfectly uniform readings of the electrometer.

The apparatus as a whole is operated in the following manner:

The pendulum R, referring again to fig. 1, is fastened by a catch Z at a position of maximum displacement from the vertical. The keys are then all closed, bringing the electrodes A and B to potential zero and closing the primary of the induction coil which operates the X-ray tube. The key D is then opened and the pendulum quickly released from the catch Z. The pendulum automatically opens the key S, giving rise to a flash of rays which ionizes the gas between the electrodes in the chamber K. Since both electrodes are at zero potential, the ions continue to recombine until the pendulum has opened the key F, when a potential is applied to the electrode A which drives over the ions of one sign remaining between the electrodes to the plate B. The earthing key is now opened and the key D closed so that the charge received on B may be measured by the electrometer.

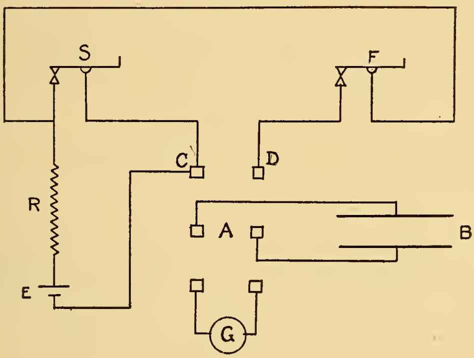
By taking a series of readings in this way with the key F at different positions along the path of the pendulum, the relative numbers of ions remaining in the gas after definite intervals of time was obtained directly. Throughout the experiment, readings were frequently repeated with the key F in such a position that the field was applied before the flash occurred, in order to detect any lack of uniformity in the action of the apparatus.

Calibration of Pendulum.

In order to ascertain the time intervals during which the ions were allowed to recombine when the switch which applied the field to the gas was placed at various positions along the path of the pendulum, the following method was used :

The switches S and F which applied the X-ray flash and the field respectively were connected as shown in fig. 2. Both switches were initially closed, and the double pole switch A was closed at CD, putting a standard condenser B in series with the switches S and F. The pendulum was then released, opening the switch S and thus permitting a storage cell E to charge the condenser through a known high resistance R. The charging continued until the pendulum opened the switch F which breaks the charging circuit. The condenser was then allowed to discharge through a galvanometer by closing the double throw switch A in the opposite direction.

FIG. 2.



The time required by the pendulum to swing from the switch S to the switch F was then computed by means of the formula

$$t = -\frac{C R \log \left(1 - \frac{q}{CE}\right)}{\log e}$$

where

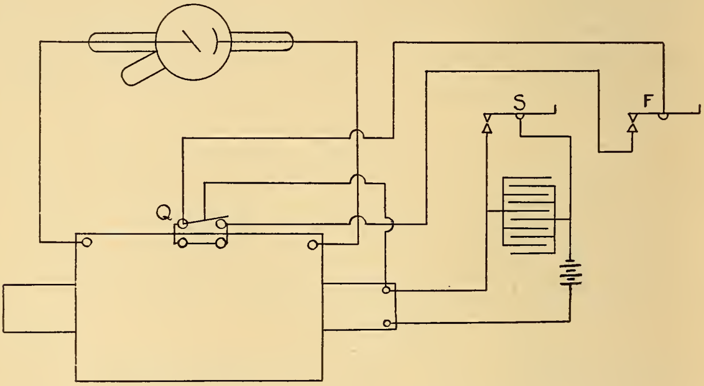
C = capacity of condenser.
q = charge received by condenser as measured by ballistic galvanometer.
E = potential of battery.
e = base of Naperian logarithms.
R = resistance in charging circuit.

The values of t obtained in this way were also checked by means of a chronograph.

The duration of the flash was obtained as follows:

In fig. 3 is shown the induction coil, X-ray tube, and keys S and F as in fig. 1, except that the key F is disconnected entirely from the potential battery system and put in parallel with a spark gap Q, which is in series with the secondary of the induction coil and X-ray tube. Q is a brass connector between the two halves of the secondary coil, and connected also to the primary coil for protection to insulation. This brass connector was removed from one binding screw to a distance of 0·5 millimeters.

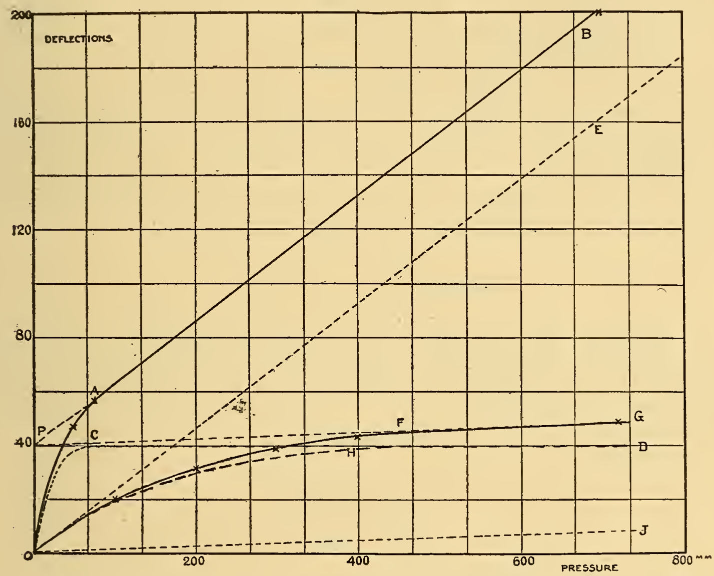
Fig. 3.



Since the connector Q is in series with the X-ray tube, a spark will occur at Q simultaneously with the flash in the tube unless the contacts of the key F are closed or so nearly closed that the discharge takes place at F instead of at Q. If when the discharge occurs the key F is closed or opened to a greater distance, no spark will be seen at F. A spark is seen at F only when the key F is so situated in the path of the pendulum with regard to the key S that the contacts of the key F are separated by a distance less than 0·5 millimeters and greater than 0 millimeters during the flash of X-rays. If it opens near the beginning of the flash, only a small spark will appear, since the discharge potential has not then attained its maximum so that when the key has opened only a short distance the resistance becomes too great and the spark ceases. On the other hand, if the key F begins to open so near the end of the duration of the discharge that when its contacts have separated only a very small distance the discharge has ceased, then again only a small spark will be observed. By placing the key F at different positions relative to S, it was found that the discharge in the X-ray tube began practically simultaneously with the opening of the key S, increased to a maximum and then fell to zero, the total duration of the flash being 0·0035 seconds. The limiting position of the key F at which the discharge ceased could be determined within a distance corresponding to 0·0001 seconds.

The calibration of the pendulum, as determined by the condenser method described above, was corrected for the time occupied by the flash by subtracting 0·0015 seconds from each value. It was necessary to know the total duration of the flash accurately also for a special experiment to be described.

Fig. 4.



Preliminary Experiment.

In order to ascertain the effect of secondary and corpuscular radiation from the electrodes A and B of fig. 1, the lead screens M M′ and N N′ were removed, allowing the Röntgen rays to fall on A and B as well as in the space between them. The plate A was charged continuously to 160 volts. Air was introduced into the chamber K and a series of deflections noted for different pressures, using single flashes of X-rays of constant intensity. The air was then pumped out and similar readings taken for hydrogen. The results are plotted in fig. 4, where the abscissæ represent pressure in millimeters of mercury, and the ordinates electrometer readings in scale divisions. It will be seen that each curve beginning at the left has a marked curvature but eventually becomes a straight line and that these two straight lines, if produced, will intersect the vertical axis in a common point.

From this it is concluded that the air curve OAB is the sum of two curves, OCD and OE, where OE is parallel to PB and OCD approaches a line through PD parallel to the pressure axis. In a similar way the curve OFG is the sum of the curves OJ parallel to PG and OHD which also approaches PD. Curves OE and OJ are due to ionization produced by the Röntgen rays in the gas, and the curves OCD and OHD are due mainly to corpuscular radiation from the plates, which is completely absorbed at a definite pressure. After replacing the lead screens MM′ and NN′ so as to confine the X-rays between the electrodes A and B, the series of readings was repeated and found to give the straight lines OE and OJ. Throughout the rest of the investigation the rays were restricted between the electrodes so as to avoid corpuscular radiation.

Experimental Results.

There is reason to believe that certain peculiar conditions are present in the initial stages of recombination. On this account it was thought advisable not to use formula (2) which involves the number of ions initially present, but to modify the formula in the following manner:

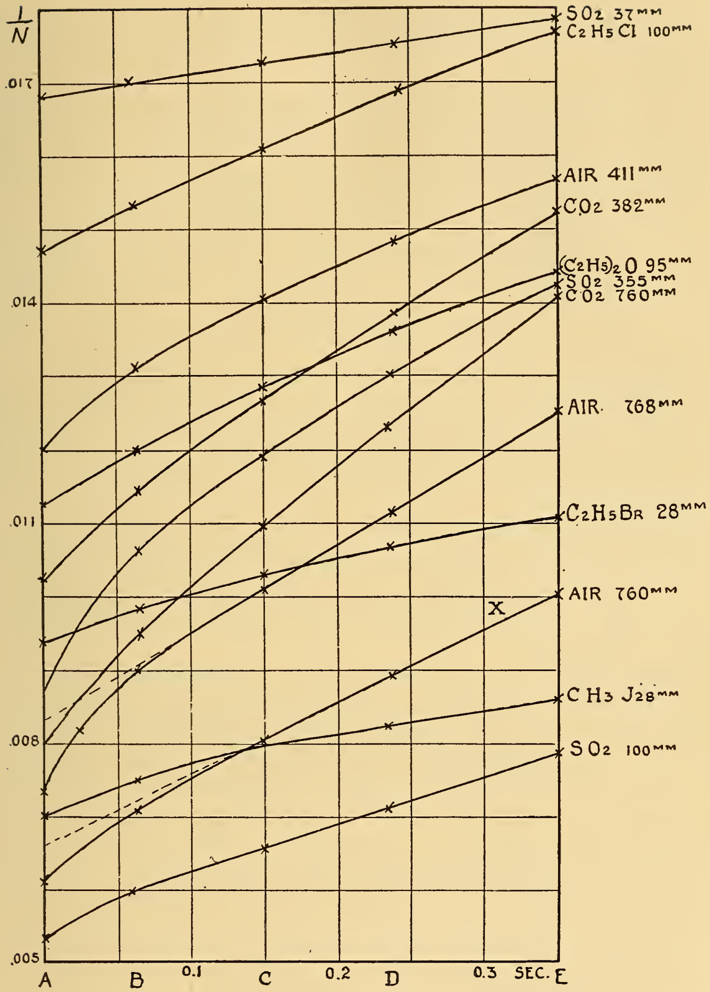
$$a = \frac{d\left(\frac{1}{n}\right)}{dt}$$

In this way the determinations of a are rendered independent of the initial conditions.

In fig. 5 the reciprocals of the deflections are plotted for the various time intervals. The slope of these curves should be proportional to a.

For short intervals of time, however, there is a marked curvature indicating that a is relatively large for the initial stages of recombination, but diminishes, becoming in most cases nearly constant for (t) greater than about one-third of a second. The curve for air is nearly straight at the end. In the case of carbon dioxide the curve is surprisingly steep at the end, indicating a very large value of a as compared with air, and one would suppose that it must ultimately become more nearly horizontal. It was, therefore, desirable to further extend the curve for air and carbon dioxide. In order to do this, the pendulum was arranged to operate the keys on the return

Fig. 5.



stroke. A key operated by hand was put in parallel with the key which applied the field and held down by hand until the pendulum was approaching the latter on the return stroke. The pendulum key was then quickly closed and the hand key released.

In this way it was possible to extend the air and carbon dioxide curves to $t = 1{\cdot}06$ seconds. The air curve was found to bend very little more, but the carbon dioxide curve became finally only a little steeper than the air curve.

Discussion of Results.

The high initial values of a and the subsequent falling off in its value, first rapidly and then more slowly, may be explained as follows:

If we suppose the action of Röntgen rays to be the liberation of rapidly moving electrons from the gas molecule, which in turn liberate slow-moving electrons from molecules in their path, thus ionizing them, one would expect the ions to be segregated in the path of the rapidly moving electrons as shown by the C. T. R. Wilson cloud experiment. This would make the value of a greater than for a uniform distribution of ionization, and, as a result of diffusion, the value of a would slowly diminish. This would probably not account for the very high initial values of a. It has been found* that the β-particle produces, on the average only about 67 ions per centimeter of path. As a rule, therefore, there must be a very large number of molecules between them, and the distance between the two ions constituting an initial pair would be, in general, less than the average distance between the ions strewn along the path of the β-particle.

If a similar condition exists in the case of ionization by the electrons expelled under the action of X-rays, there would be a relatively great probability of collision between the positive and negative ions which are close together, giving the large initial values of a.

Comparing the curves of fig. 5 for air and carbon dioxide at 760 millimeters, it will be seen that for both gases, the high initial values of a are indicated by the steepness of the curves for short intervals of time, but that the air curve becomes linear at about one-third of a second, while for carbon dioxide, the curve is very steep at this point, suggesting that it has probably not reached its final value. When the two curves were extended farther, it was found, as stated above, that these air curve remained almost linear, but that the carbon dioxide curve became almost parallel with the air curve after about two-thirds of a second. This result is in accord with the supposition that the variations in a are due to a non-uniform distribution of the ions produced by Röntgen rays. Since carbon dioxide ions diffuse only about one-half as quickly as the ions of air, the final effectively uniform distribution in which a becomes constant would be reached in carbon dioxide after about twice the time required in the case of air.

The absolute value of a.

In order to ascertain the absolute value of a at any time, it is necessary to know the number of ions present in the gas per

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* Geiger and Kovarik, Phil. Mag. (6), xxii, p. 604, 1911.

unit volume. If the ions are distributed non-uniformly as indicated by these experiments the rate of recombination at any instant would not be uniform throughout the volume, but would vary according to the density of the ions. If the distribution of the ions were known so that an average density for the total volume of the gas ionized could be computed by integration, it might be proved that a does not vary with the time. Since these data are not available the true absolute value of a cannot be computed. In the following table, the effect of a non-uniform distribution of the ions is disregarded and a is computed as if the ions were distributed uniformly by using the equation,

$$\frac{1}{n_2} - \frac{1}{n_1} = a\,(t_2 - t_1).$$

It is obvious that the values of n_2 and n_1 obtained in this way will be too small since when the ions are segregated they do not properly occupy the entire volume between the electrodes, but only a small part of that volume. The absolute values of a given in this way are therefore much too large, but diminish with the time during which the ions are allowed to recombine and diffuse since the tendency of diffusion is toward a uniform distribution.

The values given were obtained as follows:

If

$q =$ the charge which causes electrometer deflection of 1^{mm}
$e =$ the charge carried by the electron
$\text{D} =$ the electrometer deflections
$n =$ the number of ions per unit volume
$\text{V} =$ the total volume of the gas ionized;

then

$$q\text{D} = n\text{V}e \quad \text{or} \quad \frac{1}{n} = \frac{\text{V}e}{q\text{D}}$$

by equation (2)

$$a = \frac{\dfrac{1}{n_2} - \dfrac{1}{n_1}}{t_2 - t_1} = \frac{\text{V}e}{q\,(t_2 - t_1)}\left(\frac{1}{\text{D}_2} - \frac{1}{\text{D}_1}\right) = \frac{4{\cdot}07 \times (10)^5}{(t_2 - t_1)}\left(\frac{1}{\text{D}_2} - \frac{1}{\text{D}_1}\right)$$

In computing the volume V a correction was made for the distortion of the field between the electrodes due to the charge induced by the field on the insulated electrodes. This was obtained by first applying the usual field while the electrometer electrode was earthed. The earthing key was then opened and a flash of X-rays applied giving a reading of the electrometer D′. The process was then repeated in the same way except that the electrometer electrode was insulated before the field was applied, thus receiving an induced charge which distorts the field. In this instance, therefore, a smaller reading D″ was obtained owing to the distortion of the field. The corrected value of V was obtained by measuring the volume subtended between the electrodes and multiplying this by the ratio $\frac{D''}{D'}$.

The following table gives the average values of $\frac{a}{e}$ (where e is the charge carried by the electron) between the successive pairs of points A, B, C, D, E of fig. 5.

In the case of the gases air and carbon dioxide, the curves were extended to a point F where $t = 1{\cdot}06$ seconds.

Absolute Values of a/e.

Gas or Vapor	Pressure	A—B	B—C	C—D	D—E	E—F
Air	768	11540	6100	4680	4600	3960
“	411	7150	4580	3280	2820	
CO_2	760	10000	7100	6700	6500	4880
“	382	7500	6100	5610	5310	
SO_2	355	12500	7640	5150	4600	
“	100	4400	3560	2900	2830	
“	37	1560	1270	1160	1060	
CH_3I	28	3440	2540	1240	1170	
C_2H_5Cl	100	4100	4070	2870	2830	
C_2H_5Br	28	2380	2200	1850	1440	
$(C_2H_5)_2O$	95	4400	4070	3700	3180	

Effect of a Field on the Ionization.

In order to ascertain the effect of an impressed field upon the ionization, a potential of sixteen volts was applied to the gas during the flash of X-rays and removed immediately after the cessation of the flash, the recombination then being measured in the usual way.

The result is shown in curve X of fig. 5 for the case of air at 760 millimeters pressure. Comparing this with the corresponding curve for air without the application of this field during the flash, it will be seen that the final slope is not changed noticeably, but that the initial slope is lessened. This result is in accord with the explanation of initial recombination given above. The positive and negative ions in the initial pairs would be separated more widely by the field and the probabilities of collisions between them would be reduced, giving a lower value of a.

Conclusion.

(1) The recombination of ions takes place approximately in accordance with the law.

$$\frac{dn}{dt} = -an^2$$

provided that sufficient time has elapsed to enable an effectively uniform distribution of the ions to be established in the gas.

(2) When a is determined by considering a certain volume of ionized gas as a whole without regard to the distribution of the ions, a as given in the above expression is not a constant but has an initial maximum value and approaches its final constant value at first rapidly and then more slowly.

(3) An explanation of this effect is suggested based on the assumption of a non-uniform distribution of the ionization produced by Röntgen rays, the final values of a corresponding to an effectively uniform distribution.

(4) The value of a is shown to fall off as the pressure of the gas is reduced.

I wish to express my gratitude to Asst. Prof. E. M. Wellisch for suggesting these experiments, and for his very helpful interest throughout the work.

Sloane Laboratory,
Yale University,
August, 1912.

Art. VII.—*The Use of Selenic Acid in the Determination of Bromine Associated with Chlorine in Haloid Salts;* by F. A. Gooch and P. L. Blumenthal.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxxxviii]

When an aqueous solution of bromine is boiled, reaction takes place in slight degree between that element and the water, according to the equation

$$3Br_2 + 3H_2O \rightleftarrows 5HBr + HBrO_3.$$

After the greater part of the bromine has been removed from the system by boiling, a small portion may still remain, in stable equilibrium for a given concentration, as shown in the equation. In further concentration by boiling, more water and free bromine are removed, bromic acid reacts with hydrobromic acid to form bromine, according to the reverse action above, and a new equilibrium is established for each new concentration. Eventually, all the bromic acid might be reduced, and all the bromine be liberated as such, but for the fact that hydrobromic acid also tends to volatilize from the solution.

The satisfactory separation of bromine from chlorine by the action of differential oxidizers upon the haloid salts depends upon the realization of several conditions; first, the presence of a suitable reducing agent in the solution, so that if a bromate is formed, it may be instantaneously decomposed; second, the prevention of the volatilization of hydrobromic acid, by working in sufficiently dilute solution, by condensing the steam with a reflux, or by passing the vapors given off through a fresh solution of the oxidizer; third, the choice of an oxidizer which liberates bromine from bromides with the formation of a reduction product not appreciably active toward bromine under the final conditions. No substance is known which accomplishes the separation at all concentrations, and it is, therefore, necessary to select a suitable oxidizer which will decompose bromides without attacking chlorides in a solution of regulated concentrations. In such action the differential margin must be sufficiently large to admit of the practical discontinuance of the oxidation after the bromine is completely removed, and before the hydrochloric acid is attacked. The concentration of free acid in the solution is of especial importance, since it controls the rate of formation and volatilization of the halogen acids, and the rate of liberation of bromine.

Selenic acid (H_2SeO_4) may react with chlorides* and with bromides according to the reversible reactions

$$2HCl + H_2SeO_4 \rightleftarrows H_2SeO_3 + H_2O + Cl_2$$
$$2HBr + H_2SeO_4 \rightleftarrows H_2SeO_3 + H_2O + Br_2$$

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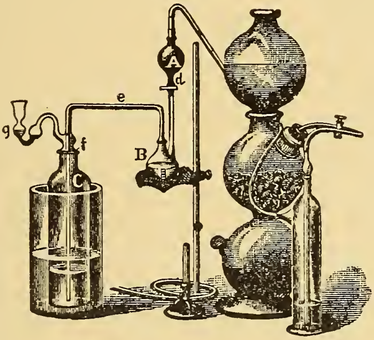
* Petterson, Zeitschr. anal. Chem., xii, 287.

Gooch and Evans* find, however, that no chlorine is liberated from solutions of small amounts of selenic acid at the boiling temperature unless the hydrochloric acid present, reckoned as concentrated aqueous acid, amounts to more than ten per cent of the entire volume. Gooch and Scoville† show that the interaction between selenic acid and potassium bromide in the presence of sulphuric acid is proportional to the acid concentration, to the bromide concentration, and to the elevation of temperature. The present paper is an account of an attempt to find conditions under which the reaction of selenic acid with chlorides shall be inappreciable while the oxidizing action upon bromides shall go to the end with the least possible reversal.

FIG. 1.



Selenic acid, now obtainable commercially, was at first used in free condition, since it is capable of performing a twofold service, that of acid, and that of oxidizing agent. Later it was found convenient to substitute a selenate with sulphuric acid to set the selenic acid free.

Solutions of iodine and sodium thiosulphate of approximately N/10 strength were carefully standardized, the iodine against the arsenic solution and the thiosulphate against the iodine, with the use of starch as the indicator. For nearly all these experiments a solution containing 3·9673 grams per liter of purest commercial potassium bromide, and 3·8974 grms. per liter of the best sodium chloride, purified by fractional precipitation from alcohol, were used in the preliminary analyses. In a few cases, the salts were weighed directly. The selenic acid employed was a commercial article of specific gravity 1·387 at 22°–23°, corresponding to that of 40·66 per cent pure selenic acid.‡

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* This Journal, [3], 1, 400. † Ibid., [3], 1, 402.

‡ Diemer and Lenher, J. Phys. Chem., xiii, p. 505.

The accompanying illustration, fig. 1, shows the apparatus used in the preliminary tests. The reaction flask was graduated at 5^{cm^3} intervals to 50^{cm^3}, the position of the meniscus being marked on a narrow slip of paper placed upon the flask or by graduation marks etched in with hydrofluoric acid. The alkali halides and 5^{cm^3} of selenic acid were introduced into the graduated flask and the total volume of liquid was made up to 50^{cm^3}. After connecting the receiver, containing 3 to 4 grms. of potassium iodide in 200^{cm^3} to 250^{cm^3} of water, carbon dioxide was slowly passed through the apparatus and the liquid in the flask, gradually heated to boiling, was kept in a state of gentle ebullition until sufficiently concentrated. In an experiment made under the above conditions, in which the bromide was omitted, 0·2000 grams of sodium chloride caused distinct coloration of the iodide in the receiver when the volume in the flask had decreased to about 20^{cm^3}, while 0·1000 grm. caused practically no color until the volume had decreased to about 10^{cm^3}. In the following experiments in which the bromide was associated with chloride, therefore, the amount of sodium chloride was restricted and the final concentration was kept above the limit at which the attack upon the chloride begins. The flask was cooled and disconnected, and the free iodine in the receiver was titrated and taken as the measure of the bromine. Afterward, when the chlorine was to be estimated, connection was made with the receiver freshly charged with iodide and the distillation was continued to secure the evolution of the chlorine, which was estimated by titration of the iodine set free in the second distillation. The results follow in Table I.

The figures for bromine are rather low and somewhat irregular, while those for chlorine, although the concentrations are carried below the point at which the selenic acid itself begins (as was shown in blank tests) to liberate iodine in the receiver, are very irregular and generally low. It does not seem to be feasible to adjust the process so that the chlorine may be estimated by a second distillation, after the removal of the bromine. In the following experiments, therefore, attention was given exclusively to the determination of bromine.

The potassium bromide used in the following experiments was prepared for use from the purest available bromate by ignition, thorough fusion, pouring out upon platinum, cooling, powdering, drying at 105°, boiling and keeping in a sulphuric acid desiccator. A part of this material when dissolved in hot water recrystallized, dried between filters and afterward at 100° and analyzed by the gravimetric silver nitrate process, showed no variation in composition in consequence of this treatment. The results obtained with the bromide alone, and with that substance associated with sodium chloride, are given in Table II.

Table I.

Preliminary Tests with Selenic Acid, Potassium Bromide, and Sodium Chloride.

KBr taken grm.	NaCl taken grm.	H_2SeO_4 taken (40·66%) cm³.	Initial volume cm³.	Volume for bromine cm³.	Volume for chlorine cm³.	KBr found grm.	Error in terms of KBr grm.	NaCl found grm.	Error in terms of NaCl grm.
----	0·2000	5	50	20	---	color	----	----	----
----	0·1000	5	25	11	---	color	----	----	----
0·1000	----	5	55	24	---	0·0979	—0·0021	----	----
0·2000	----	5	58	16	---	0·1968	—0·0032	----	----
0·0988	0·0970	5	--	25	2–3	0·0985	—0·0003	0·0949	—0·0021
0·0990	0·0972	5	48	18	3–4	0·0985	—0·0005	0·0955	—0·0017
0·0793	0·0779	5	--	17	--	0·0788	—0·0005	0·0745	—0·0034
0·1389	0·1364	5	55	17	3	0·1380	—0·0009	0·1364	0·0000
0·1389	0·1364	5	55–60	12	1–2	0·1383	—0·0006	0·1377	+0·0011
0·0793	0·0779	5	40	17	---	0·0785	—0·0008	----	----
0·0991	0·0973	5	70	15	1–2	0·0984	—0·0007	0·0966	—0·0007

Table II.

The Determination of Bromine liberated by Selenic Acid.

Br taken as KBr grm.	NaCl taken grm.	H_2SeO_4 (40·66%) taken cm³.	Initial volume cm³.	Final volume cm³.	Br found grm.	Error in terms of Br grm.
0·0749	....	5	40	15	0·0721	—0·0028*
0·0671	....	5	50	13	0·0762	—0·0009*
0·0671	....	5	55–60	6–7	0·0760	—0·0011*
0·0671	....	5	50	15	0·0758	—0·0013*
0·0673	....	5	50	16	0·0765	—0·0008†
0·0671	....	5	-	12	0·0758	—0·0013†
0·0685	....	5	50	24	0·0672	—0·0013†
0·2364	0·1757	5	40	11	0·2332	—0·0032‡
0·2026	0·1507	5	40	7–8	0·2016	—0·0010‡
0·1688	0·1255	5	40	7–8	0·1677	—0·0011‡
0·1350	0·1003	5	30	7	0·1340	—0·0010‡
0·1350	0·1003	5	30	9	0·1345	—0·0005‡
0·1350	0·1003	5	30	12	0·1348	—0·0002‡
0·1350	0·1003	5	30	12–13	0·1346	—0·0004‡
0·1013	0·0753	5	25	11	0·1006	—0·0007‡

* The bromide, made from the bromate, was fused and weighed out in each case.

† The bromide, made from the bromate, was fused, recrystallized, dried, and weighed out in each case.

‡ The bromide, made from the bromate, was made up with sodium chloride in a solution from which aliquot portions were measured.

As in the preliminary tests of Table I, these results run low for bromine, with considerable fluctuations.

An experiment showed that the flask residues of selenic acid, selenious acid, and the potassium salts of these acids were capable of reducing minute amounts of bromate, and of liberating bromine at the boiling temperature. Therefore, the larger of the deficiencies observed cannot be wholly attributed to the retention of bromine in the form of bromic acid or a bromate. Apart from the possibility of trifling losses of liberated iodine due to mechanical transfer in the current of carbon dioxide, the most reasonable explanation of irregularity in results would seem to be the escape of some hydrobromic acid from the reaction flask, without undergoing oxidation. In the subsequent work, therefore, the apparatus was modified to the form shown in fig. 2, so that the vapors escaping from the reaction flask (I) might be forced through another portion of selenic acid, kept hot in a relay flask (II), before passing to the receiver. The selenic acid in the relay flask was kept at 100°

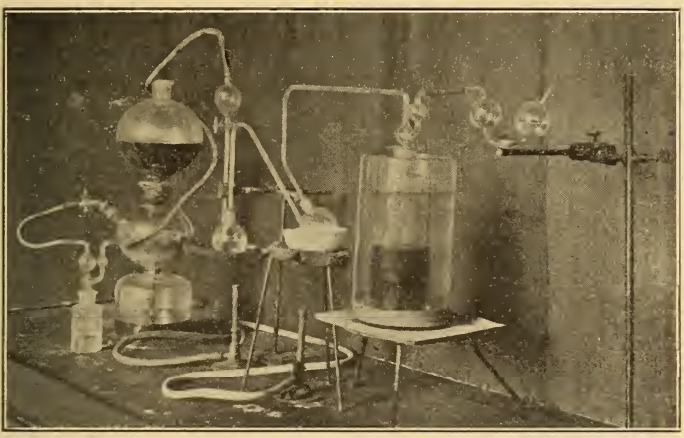
to 110° by means of an oil bath heated to 120° to 130°. The details of experiments with this apparatus are given in the following table:

TABLE III.

Tests with Selenic Acid, and the Relay Apparatus.

Br taken as KBr grm.	Taken NaCl grm.	H_2SeO_4 I cm³.	H_2SeO_4 II cm³.	Final volume in reaction flask cm³.	Br found grm.	Error grm.
0·0675	0·0050	5	2·5	12–13	0·0671	–0·0004
0·1350	0·0050	5	2·5	15	0·1339	–0·0011
0·1013	0·0050	5	2·5	12–13	0·1003	–0·0010
0·0675	0·1505	5	2·5	15	0·0672	–0·0003

FIG. 2.



So far as may be judged from the few results of Table IV, the use of the second voit flask to repeat the contact with selenic acid is favorable, and this evidence is confirmed in the work which follows, in which sulphuric acid and a selenate were used to generate the selenic acid in the reaction flasks. There is still a constant error of deficiency in the bromine. averaging 0·0007 grm., which might suggest that, in reversal of the fundamental reaction by which bromine is set free, the reoxidation of selenious acid by bromine is a possibility even at the final concentration. If this were the case, the addition of more selenic acid and further concentration of the solution in the reaction flask should advance the main reaction; but the addition of 5^{cm^3} more of the selenic acid after the estimation of the bromine, and repetition of the boiling to almost the limits at which chloride begins to be evolved, resulted in no appreciable improvement in the results by further evolution of bromine. It must be concluded that the reaction by which selenic acid sets free the bromine is complete under the conditions, or else that the supplementary amount of selenic acid is inadequate to change perceptibly the equilibrium established in the first boiling.

In experiments to be described the conditions of action were somewhat changed by using sulphuric acid and a selenate, in the place of free selenic acid, to effect the liberation of the bromine. The sodium selenate used was prepared in the laboratory and was contaminated with sodium sulphate, though otherwise pure. The selenate content was, however, determined and a solution of the mixed salts was prepared of such strength that 10^{cm^3} contained 1 grm. of sodium selenate. A preliminary series of experiments was made to determine the conditions suitable to the use of this reagent. It was found that chlorine is evolved from sodium chloride in presence of sulphuric acid at concentrations much lower than those at which the evolution begins when free selenic acid is the oxidizer in absence of sulphuric acid. The effects observed are shown in Table IV.

TABLE IV.

Concentrations of Sulphuric Acid, Selenate, and Chloride at which the Evolution of Chlorine begins.

NaCl taken grm.	Na_2SeO_4 taken grm.	H_2SO_4 (1 : 1) taken cm³.	Volume of the reaction liquid at which color appears in the receiver cm³.
0·1004	0·6	12	35–40
0·0753	0·6	12	30–35
0·0500	0·6	12	20–22
0·0500	0·6	6	16
0·0500	0·6	3	8–9
0·0500	1·8	3	9

The results of similar preliminary experiments with potassium bromide are shown in Table V.

A comparison of the results of Tables IV and V shows that with 3^{cm^3} of sulphuric acid (1 : 1), 1·8 grm. of sodium selenate, and 0·05 grm. of sodium chloride in the reaction flask (I), the concentration may safely reach a volume of 10^{cm^3}. Determina-

TABLE V.

The Evolution of Bromine by Sulphuric Acid and Sodium Selenate.

Br taken as KBr grm.	Na_2SeO_4 taken grm.	H_2SO_4 (1 : 1) grm.	Final volume cm^3.	Br found grm.	Error grm.
0·1041	1·2	12	15–16	0·1029	—0·0012
0·1041	1·2	12	13–14	0·1033	—0·0008
0·0694	1·2	12	17–18	0·0686	—0·0008
0·0694	1·2	12	16–17	0·0692	—0·0002
0·0694	1·2	12	16–17	0·0691	—0·0003
0·0694	0·6	12	12–13	0·0691	—0·0003
0·0694	0·6	6	11–12	0·0691	—0·0003
0·0694	1·8	3	12–13	0·0689	—0·0005
0·0694	1·8	3	12	0·0691	—0·0003
0·0694	1·8	3	12	0·0689	—0·0005
0·0694	1·8	3	10	0·0691	—0·0003
0·0694	0·6	3	11–12	0·0669	—0·0025

tions of the bromine in potassium bromide associated with sodium chloride, made under these conditions, are recorded in Table VI. In these determinations the relay flask (II) was used, charged with 1^{cm^3} to 2^{cm^3} of sulphuric acid (1 : 1), 0·2 grm. to 0·3 grm. of sodium selenate, and 10^{cm^3} to 15^{cm^3} of water.

TABLE VI.

Determination of Bromine by Selenate-Sulphuric Acid Process.

Br taken as KBr grm.	NaCl taken grm.	Na_2SeO_4 taken I grm.	II grm.	H_2SO_4 (1 : 1) taken I cm^3	II cm^3	Final volume I cm^3	Br found grm.	Error grm.
0·0694	0·0500	1·8	0·2–0·3	3	1–2	14	0·0683	—0·0011*
0·0694	0·0500	1·8	0·2–0·3	3	1–2	13–14	0·0690	—0·0004
0·0694	0·0500	1·8	0·2–0·3	3	1–2	13–14	0·0690	—0·0004
0·0694	0·0500	1·8	0·2–0·3	3	1–2	12–13	0·0693	—0·0001
0·0694	0·0500	1·8	0·2–0·3	3	1–2	12–13	0·0693	—0·0001
0·0694	0·0500	1·8	0·2–0·3	3	1–2	11	0·0692	—0·0002
0·0694	0·0500	1·8	0·2–0·3	3	1–2	11	0·0683	—0·0011
0·0694	0·0500	1·8	0·2–0·3	3	1–2	10	0·0692	—0·0002

* CO_2 was passed for a considerable time after cooling.

The average error in these determinations is 0·0004 grm. in terms of bromine.

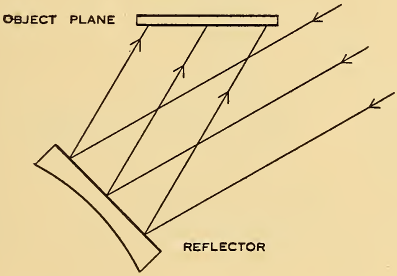
According to the procedure which we have found to be effective for the amounts of material dealt with, the haloid salt is introduced into the reaction flask with 30^{cm^3} of water. Selenic acid, 5^{cm^3} of 40 per cent acid, or the mixture of 1·8 grm. of sodium selenate with 3^{cm^3} of sulphuric acid (1 : 1), is diluted with 20^{cm^3} of water and put into the separatory funnel. Into the relay flask are put $2·5^{cm^3}$ of selenic acid and 10^{cm^3} to 15^{cm^3} of water, or 0·2 grm. to 0·3 grm. of the selenate with 1^{cm^3} to 2^{cm^3} of the (1 : 1) sulphuric acid and 10^{cm^3} to 15^{cm^3} of water. The relay flask is heated in the oil bath kept at 115° to 120°. The receiver is charged with 3 grm. to 4 grm. of potassium iodide dissolved in 200^{cm^3} to 250^{cm^3} of faintly acidified water, and set in a jar of cold water. The apparatus is connected (as shown in fig. 2), the dilute sulphuric acid is allowed to run into the reaction flask, and a slow current of carbon dioxide replaces the air in the apparatus. The reaction flask is heated until the liquid boils gently, while the oil bath which heats the relay flask is kept at 115° to 120°. The reaction mixture is boiled gently until diminished to a volume of 10^{cm^3} to 15^{cm^3}, when the source of heat is withdrawn and carbon dioxide is passed in a current of sufficient rapidity to prevent back suction of the liquid in the receiver, but regulated to the lowest convenient limit, in order that iodine may not be swept from the receiver and lost to estimation. After the flasks are cool enough to be handled conveniently the apparatus is disconnected, the contents of the receiver and safety bulb are united, and the free iodine is titrated with standard sodium thiosulphate and taken as the measure of the bromine evolved. The entire operation need not occupy more than fifty minutes, and, with practice, may be shortened to forty minutes.

With selenic acid as the active agent it is possible to determine, under the conditions defined, the bromine of 0·25 grm. of bromide in association with 0·15 of chloride in the haloid salts. With sodium selenate and sulphuric acid to bring about the reaction, the separation is shown to be regular and fairly accurate for 0·07 grm. of bromine associated with 0·05 grm. of chlorine in the haloid salts. What the accuracy of the process may be when larger amounts of the salts are handled remains to be determined.

ART. VIII.—*Oblique Illumination in Petrographic Microscope Work;* by FRED. EUGENE WRIGHT.

IN ordinary microscope work three kinds of illumination are in common use—central, oblique, and dark-ground. Of these the last is employed only with high magnifications and then to emphasize the outlines of minute particles. It is rarely applied to petrographic microscope work because of the relatively low magnifications there required. Oblique illumination is also often disregarded by petrologists, who employ central illumination either by parallel or convergent light to the practical exclusion of all other types. There are many instances, however, where oblique illumination is better adapted to bring out certain optical phenomena than either central or dark-ground illumination and where it should accordingly be adopted. In the following paragraphs it is proposed to indicate a few of these uses and to explain briefly certain details of the methods which, in part at least, seem not to have been considered heretofore.

FIG. 1.



Methods for Producing Oblique Illumination.

(1) By swinging the substage mirror to one side and allowing the light to enter the section under a large angle (condenser and polarizer having been previously removed);

(2) by a sliding stop in the lower focal plane of the condenser;

(3) by placing the index finger below the condenser and observing the edge of the shadow which it casts;

(4) by means of an opaque strip immediately above the upper lens of the condenser;

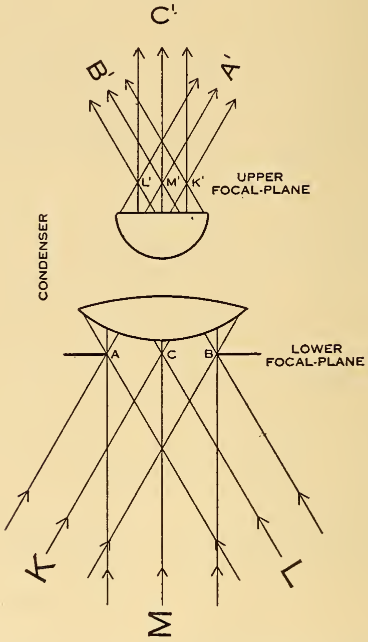
(5) by use of a sliding stop in the microscope draw tube;

(6) by a sliding stop in the eye circle of the ocular.

These different methods will now be considered briefly and with special reference to their suitability for use in practical work.

(1) In this method, which has frequently been used,* the condenser and polarizer are first removed from the microscope and the mirror swung to one side from which the reflected beams of light enter the section under an incident angle of 50° under favorable conditions (fig. 1). If the polarizer be allowed to remain on the microscope, this angle of incidence is materially decreased (to less than 15°) unless the nicol carriage be specially constructed so that it can be swung together with the mirror.†

Fig. 2.



For practical work this method for obtaining oblique illumination is hardly to be recommended in view of the bother connected with its application. It does, however, furnish a fairly parallel beam of light under a relatively large angle provided the nicol and condenser are not present on the microscope. The intensity of illumination obtained under these conditions is not great.

* Schroeder van der Kolk, Zeitschr. Wiss. Mikroskopie, viii, 456–458, 1892.

† Schroeder van der Kolk, ibid., viii, 458, 1892.

(2) The principle on which the second method is based is illustrated in figs. 2 to 5.

In fig. 2 the paths of parallel beams of rays entering the condenser under different angles of incidence are shown. Such beams are readily obtainable and their significance most easily appreciated by using the plane side of the substage mirror and observing distant points on the horizon as they appear reflected in the mirror. The parallel beams of light are brought to focus by the condenser in its upper focal plane where the distant points K, L, M are imaged at K′, L′, M′. From the figure it is evident that the greater inclination of an incident beam of light the farther from the central axis does it come to focus; conversely, points near the center of the field, K′, L′, M′ are formed by beams of light incident under relatively small angles.

Fig. 3.

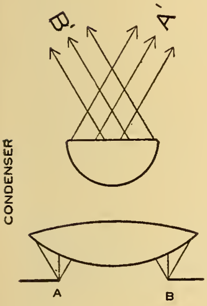


Fig. 4.

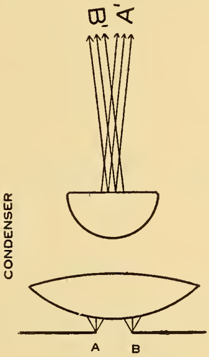
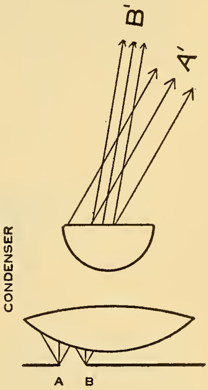


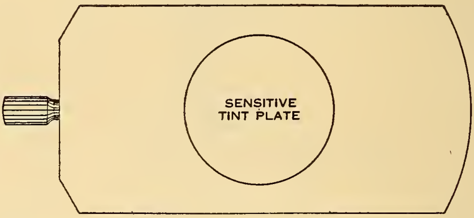
Fig. 5.



This relation has an interesting bearing on the object field of view of objectives. In modern objectives, the shorter their equivalent focal length (E. F.) the smaller their object field of view, and hence the smaller the angle of the incident cone of illumination required to cover the field, and vice versa; in general, the longer the E. F. of an objective the greater the angle of the cone of incident illumination required for the same condenser; for the same cone of illumination, the longer must be the E. F. of the condenser to increase the width of cone of illumination in the object field. For this reason the large Abbe condensers with relatively long E. F. can be used for observations both in parallel and in convergent polarized light without disturbing the upper lens of the condenser system; but with such large condensers correspondingly large polarizers are required. The relation between the actual width of the upper focal plane of the condenser (image plane for incident beams of parallel light) and the angle of the cone of illumination is often disregarded, but is fundamental to a clear understanding of the function of the condenser in petrographic microscope work.

Still another point requires explanation. In figs. 3 and 4 the effect of closing the iris diaphragm in the lower focal plane of the condenser is illustrated. This case is practically the converse of that considered in the last paragraph. By closing the iris diaphragm we decrease the angle between the emergent beams; in short, we reduce the numerical aperture of the condenser. By shifting the small opening AB as in fig. 5 we obtain a narrow bundle of obliquely emergent rays. These rays are not strictly parallel but form a narrow cone whose angle of opening is so small that it is negligible in microscope work. To obtain obliquely incident light by this method it is best to employ a sliding iris diaphragm; but almost equally good results can be obtained by using a sliding stop or metal strip in the lower focal plane of the condenser;* a good substitute for such a stop

Fig. 6.



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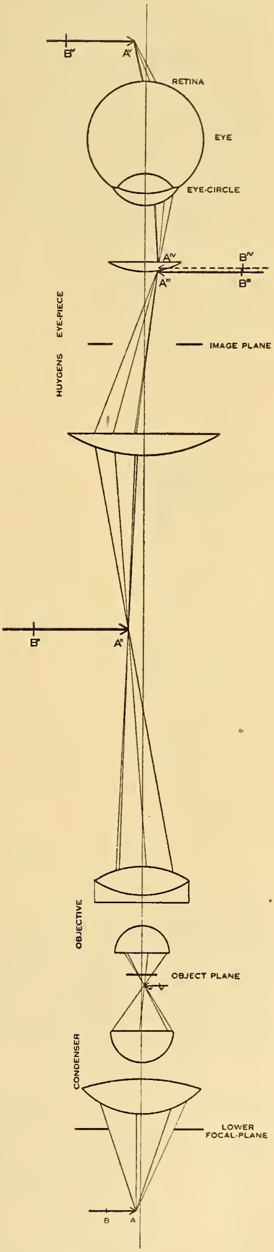
* A simple device has been used by the writer and found satisfactory in practice. In the lower focal plane of an aplanatic condenser (n.a. $=1{\cdot}4$) a glass coördinate scale is inserted, which gives directly the angle of inclination of the emergent rays; this scale is used primarily for the direct measurement of optic axial angles. Directly below the scale an iris diaphragm is inserted, so that its plane practically coincides with that of the glass scale. Attached to the projecting base of the condenser and supporting the iris diaphragm is a collar into which a brass slider fits below the iris diaphragm; this slider serves two purposes: (1) as a sliding stop or strip to produce oblique illumination; (2) as a frame for a large sensitive tint plate (fig. 6). The supporting collar together with iris diaphragm can be rotated and allows the observer to obtain obliquely incident light in any azimuth, and also to insert the sensitive tint plate so that its ellipsoidal axes include any given angle with the principal nicol planes. This last feature is especially important for the examination of fine, weakly birefracting grains, because it enables the observer to rotate the sensitive tint plate to a position where its ellipsoidal axes almost coincide with the principal nicol planes. The field illumination resulting from the sensitive tint plate is then hardly perceptible, while the change in interference tint from red to blue or yellow is clearly marked in the minute mineral plate in the diagonal position. When the sensitive tint plate is inserted in the usual diagonal position the intensity of illumination of the field is so great that the delicate interference tints from the minute grains are completely veiled and lost to view. These statements apply with equal force to observations in convergent polarized light, especially to the determination of the optical character of thin, weakly birefracting plates. (See F. E. Wright, Methods of Petrographic-Microscopic Research. Carnegie Institution of Washington, Pub. 158, 73, 1911.)

is the index finger placed below the condenser in such a position that it allows only marginal rays to enter at one side of the condenser. In this manner a bundle of rays incident on the section under a high angle and in any azimuth can be readily obtained; if, for any special purpose, rays of a given angle of emergence are required, they can be had by using a small sliding stop (iris diaphragm), but such instances are rare and the index finger is satisfactory for all practical purposes.

(3) This method is similar to the second in principle but slightly different in its details. In this method the index finger or a sliding stop below the polarizer* is used and serves to cast a shadow over part of the microscopic field. The path of the rays under these conditions is illustrated in fig. 7, in which the finger or sliding stop is represented by the arrow AB. AB is imaged by the condenser at $A^{I}B^{I}$, by the objective at $A^{II}B^{II}$, by the field lens of the ocular at $A^{III}B^{III}$, by the eye lens of the ocular at $A^{IV}B^{IV}$, and by the eye at $A^{V}B^{V}$ behind the retina. In fig. 7 the microscope is focussed on the object plane and the image $A^{V}B^{V}$ does not appear, therefore, in sharp focus (coincide with the retina), but rather as a dark shadow with wide blurred edges. It is with these semi-dark edges that the method has to do.

In figs. 8, 9, 10 these relations are shown on a larger scale than in fig. 7, and for the condenser part of the microscope system only. In fig. 8 the condenser is in such a position that the object AB is sharply imaged in the object plane of the draw-tube lens system; under these conditions the edge of the finger or sliding stop

Fig. 7.



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*F. E. Wright, Min. petr. Mitt., xx, 239, 1901; this Journal (4), xvii, 385–387, 1904.

is viewed simultaneously and in sharp focus with the object. No blurred edges are visible. If now the condenser system be lowered (fig. 9) or raised (fig. 10), the finger edge becomes indistinct and blurred. The paths of the rays are indicated in the figures and require no further explanation.

If now a mineral grain (indicated as of irregular outline in the object plane of the figures) be observed with the condenser and finger in the position of fig. 8, it appears illuminated by light from all directions and no effects of oblique illumination are visible. In fig. 9, however, the rays which impinge on it are included in the indistinct edge of the shadow and these travel from left to right in the figure, while in fig. 9 their direction is from the opposite side, right to left; but in both cases oblique illumination is obtained, though not over so large an area as in the second method.

Fig. 8.

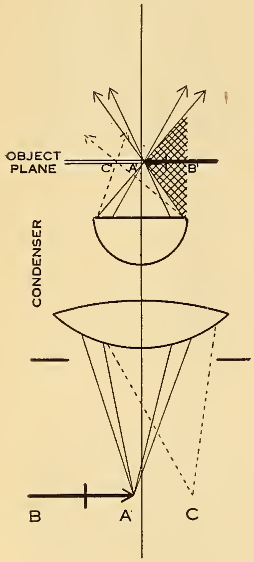


Fig. 9.

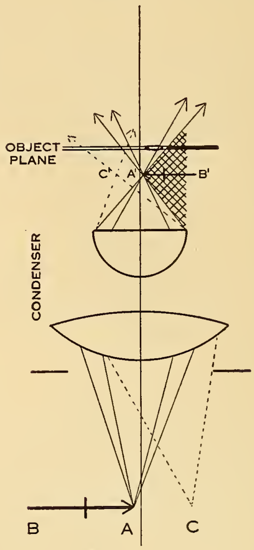
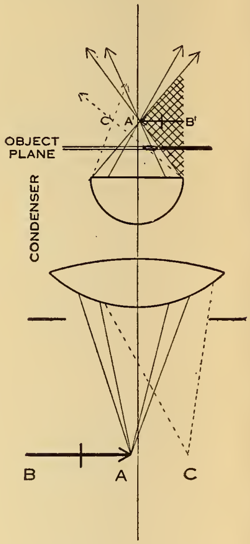


Fig. 10.



(4) This method was first used by Schroeder van der Kolk,* who placed a metal strip over the upper lens of the condenser as indicated in fig. 11. From this figure it is evident that the oblique illumination obtained by this method is less perfect than that of the foregoing methods. There is a greater number of rays from one particular direction which are not cut off,

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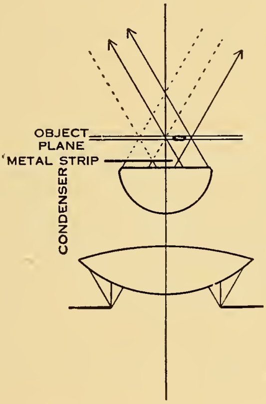
*Zeitschr. Wiss. Mikroskopie, viii, 456–458, 1892; Kurze Anleitung zur mikroskopischen Krystallbestimmung, Wiesbaden, 1898.

but there are also rays which reach the section from other directions. The fact that rays from one direction preponderate gives rise to the characteristic phenomena produced by obliquely incident light while the remaining rays only tend to veil these phenomena and to render them less distinct. In this respect this method is inferior to the first three methods.

(5) When the condenser is focussed on the object plane of the draw-tube system, the lower focal plane of the condenser is conjugate to the upper focal plane of the objective (fig. 7); a stop placed in the upper focal plane of the objective functions, therefore, similarly to a stop in the lower focal plane of the condenser,* and if properly placed should produce equally satisfactory oblique illumination. In actual practice, however, this method is not satisfactory because of the difficulty of inserting the stop in the upper focal plane of the objective. This focal plane, moreover, is not a plane but a warped surface and covers only a small area. In many objectives the upper focal plane is located within the lens system and is accordingly out of reach entirely. In low power objectives of small numerical aperture, moreover, the angle of inclination of the most obliquely incident rays attainable is too small to be of much service. In view of these objections the method can hardly be recommended for general use.

Fig. 11.



(6) In fig. 7 the image $A^{II}B^{II}$ is conjugate to AB, and a stop placed at $A^{II}B^{II}$ should function similarly to AB itself. Theoretically this statement may be true, but practically it does not

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* H. Ambronn (Ber. Sächs. Gesell. d. Wissen. Math. phys. Kl., 1896, 1–6) has developed a method for measuring relative refractive indices, which is based on the phenomena produced in the upper focal plane of the objective.

hold. The angle of inclination of the rays within the draw tube is so small (less than 3°) that it is difficult to place the stop in a position to show the phenomena clearly. The edge of the shadow thus obtained is furthermore very narrow. In case a low power objective be used, the object itself is usually illuminated by a cone of rays whose angular aperture is so large that they cannot all enter the objective; they produce, however, phenomena of refraction in the object which are readily imaged through the objective but which cannot be produced by stops within the draw tube. This objection applies to all methods involving stops placed above the object itself, whether in the draw tube or above the ocular as in the method described below.

(7) In the properly focussed microscope system the eye circle is the conjugate image of the lower focal plane of the condenser (fig. 7). A stop in the lower focal plane of the condenser is accordingly imaged in the eye circle of the ocular, and vice versa. In view of this mutual relation one might well conclude that it is immaterial whether a stop be used in the eye circle or in the lower focal plane of the condenser for producing oblique illumination, but actual practice proves this to be not strictly true, partly for the reasons cited under (6) above and partly because of the imperfections in the lens system which is not corrected primarily for the eye circle; the result being that, because of cumulative errors, an object in the lower focal plane of the condenser is imperfectly imaged in the eye circle, and the difficulty of properly placing a stop there is greatly increased. This method, however, has often been suggested* for producing oblique illumination, but it has not been actually used to any great extent by petrographers. It is inferior, both theoretically and practically, to methods (2) and (3) described above.

Recapitulation.— In the above paragraphs the different feasible methods for obtaining oblique illumination with the petrographic microscope are described and their relative merits briefly considered. From the discussion it is evident that the methods are not all equally good either from a theoretical or from a practical standpoint. Theoretically the first three methods are superior to the others, and methods (2) and (3) are also simplest to apply in actual work. They should, therefore, be adopted in preference to the others.

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*S. Exner, Archiv Mikroskop. Anat., xxv, 97, 1885; F. Becke, Sitzungsber. Acad. Wien, I Abt., cii, 358–376, 1893; Min. petr. Mitt., xiii, 385–388, 1893; J. W. Gordon, see Spitta, Microscopy, p. 179, 1909; F. E. Wright, Carnegie Inst. Washington, 158, 95, 1911; H. Schneiderhöhn, Zeitschr. Kryst., l, 234, 1912.

THE USES OF OBLIQUE ILLUMINATION IN PETROGRAPHIC MICROSCOPE WORK.

Determination of the relative refractive indices of adjacent mineral grains or of mineral grains immersed in liquids.

Let us first consider the principles on which the immersion method for determining the refractive indices of mineral grains is based. This method has been frequently described, but it is so useful that it cannot be too strongly emphasized. It is founded primarily on two physical facts, the refraction of light and the relative color dispersion between liquids and solids.

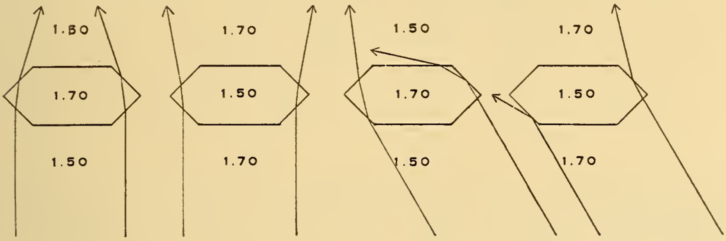


FIG. 12*a*. FIG. 12*b*. FIG. 12*c*. FIG. 12*d*.

The relations which result from these facts are illustrated in figs. 12 to 17, in which the mineral grain is considered immersed in liquids of different refractory indices. Figs. 12*a*, 12*c*, 13*a*, 13*c* are drawn for the case that the refractive index of the mineral is 1·70 and that of the liquid 1·50. In figs. 14*a*, *b*, the refractive indices of the mineral are: 1·542 for the wave length 650$\mu\mu$; 1·546 for $\lambda = 550\mu\mu$; 1·552 for $\lambda = 450\mu\mu$, while for the liquid they are 1·535 for $\lambda = 650\mu\mu$; 1·546 for $\lambda = 550\mu\mu$; 1·570 for $\lambda = 450\mu\mu$; the refractive indices of mineral and liquid are equal for the wave length $\lambda = 550\mu\mu$, but the liquid has a lower

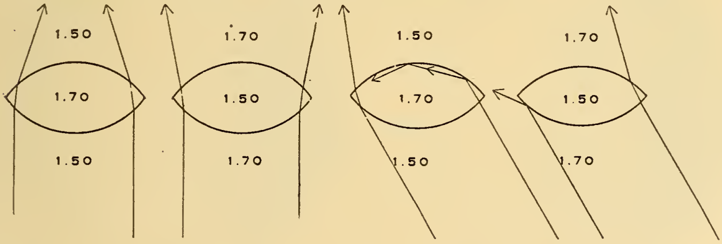


FIG. 13*a*. FIG. 13*b*. FIG. 13*c*. FIG. 13*d*.

index for the red end of the visible spectrum and a higher index for the blue and green rays.

Fig. 14*a*.

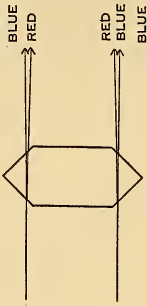


Fig. 14*b*.

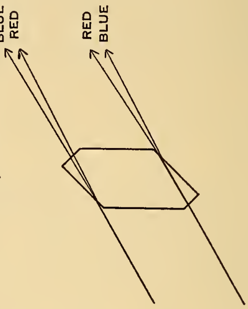


Fig. 15.

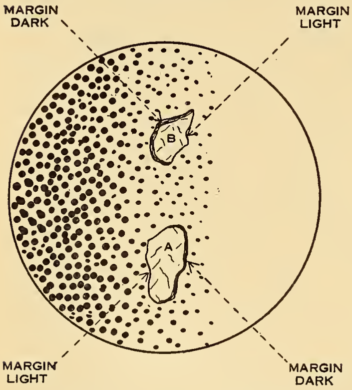
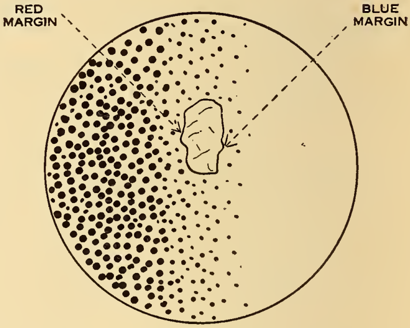


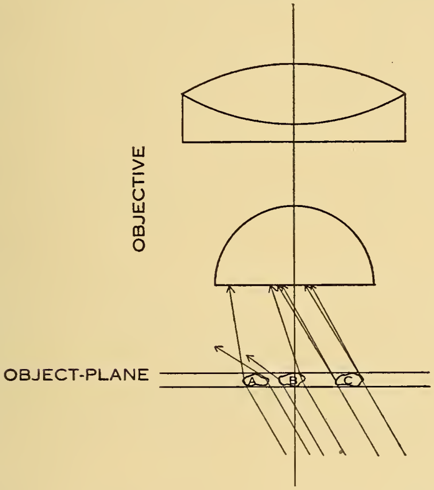
Fig. 16.



Figs. 12 to 17 are drawn on the assumption that the margins of the immersed mineral grain are more or less wedge-shaped (prismatic) or lenticular; theoretically these two cases are not different because any warped or curved surface can be considered as resolved into a succession of very minute plane surface elements. In practical work the above assumption of more or less wedge-shaped margins on mineral grains is valid and the relations depicted in figs. 12 to 17 obtain. In figs 12*a* and 13*a* the mineral has a higher refractive index than the surrounding liquid and a beam of centrally incident parallel light emerges from the grain as a convergent bundle, while in figs. 12*b*, 13*b* a similarly incident beam emerges as a divergent bundle. In case the microscope be first focussed on the margin of the grain AB and then raised, the intensity of the field illumination is found to change continuously—the rays being concentrated toward the center of the grain in figs. 12*a* and 13*a* where the mineral has the higher index, while in figs. 12*b* and

13*b* the reverse is the case, the zone of maximum illumination receding from the center of the grain on raising the draw tube.* In figs. 12*c*, 13*c* the effect of oblique illumination on the higher refracting mineral grain is indicated. Under such conditions opposite margins of the mineral grains appear unequally illuminated, the rays from the margin on the right emerging at such a large angle that they fail to enter the objective (fig. 17, grain A), while from the margin on the left the rays do enter the microscope. The left margin appears, therefore, brightly illuminated while the right margin is relatively dark. The greater the difference in refractive index between liquid and mineral grain, the more pronounced is this contrast in illumination and the more the grain stands out in relief. In figs. 12*d* and 13*d* the mineral grain has the lower refractive index and dark and light margins appear reversed, the right margin being now bright and the left margin dark. These relations are indicated in fig. 15 and in fig. 17 (grains A and B), and are sufficiently obvious without further comment; they enable the observer to determine at once whether the mineral grain has a higher or lower refractive index than the enclosing liquid.

FIG. 17.



In case the mineral grain and liquid have the same refractive index for some wave length near the center of the visible spectrum (about $550\mu\mu$), the greater color dispersion of most liquids

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* O. Maschke, Pogg. Ann. Phys. Chem., cxlv, 568, 1872; Wied. Ann., xi, 722, 1880; F. Becke, Sitzungsber. Akad. Wien, I Abt., cii, 358, 1892; Min. petr. Mitt., xiii, 385, 1893; A. Brun, Arch. Soc. Phys. et Math., Généve, xxxii, 3, 1894.

over solids enters the problem and gives rise to characteristic color fringes along the margins of the mineral grain. Under these conditions the mineral has a higher refractive index than the liquid for the red rays, while for the blue rays the liquid has the higher refractive index, with the result that the red rays emerge as a convergent bundle (figs. 12*a* and 14*a*) while the blue rays are divergent (fig. 12*b*, 14*b*). This difference in behavior between the blue and red rays can be clearly seen on properly immersed grains illuminated by a narrow central cone of light from the condenser; on raising the objective, a red marginal line appears to move toward the center of the grain while a similar blue marginal line moves out and away from the center.

These marginal fringes can be studied to still better advantage on grains illuminated from a strong point source of light (Nernst glower) placed approximately in the plane of the substage reflector, the condenser and reflector having been previously removed; the dispersion colors obtained with this arrangement are remarkably clear and beautiful. By shifting the Nernst glower to one side oblique illumination can be obtained and characteristic phenomena produced (fig. 14*b*, 17C) which are best shown by a low power objective (E.F. about 16^{mm} and N.A. 0·65). On shifting the Nernst glower away from the axis of the microscope we soon reach a limit beyond which direct light no longer enters the objective (limit of angular aperture of objective in object field); this limit is not sharp, but a hazy, transition edge, grading into the bright field on the one side and into the black, non-illuminated field on the other. It is in this semi-dark transition zone that the phenomena of color dispersion are best observed. In fig. 14*b* the effect of the color dispersion between a mineral grain and the enclosing liquid are illustrated (the drawings are angle-true for the refractive indices given above on page 71); the angle between the blue and red rays on emergence is 4° 57′ at the right margin of the grain and 3° 36′ at its left margin. In view of the small angle between these rays it might seem difficult to explain why the dispersion colors are so clearly marked along the margins of the grains. But the reason is obvious when we note that these colors are practically confined to the semi-dark zone between darkness and light in the field. This narrow zone is itself less than 5° in width, and in it correspondingly small angular differences between entrant rays are rendered visible. Thus in the grain of 14*b* the red rays from the left margin are less steeply inclined than the blue rays and would accordingly be transmitted and visible through an objective whose angular aperture is just large enough to admit them but too small to admit the blue rays. Under these conditions the left margin of the grain would appear tinged with red. For the right margin, on the other hand, the blue rays are less steeply inclined and this margin would accordingly be blue under these conditions. By shifting the Nernst glower the angle of the incident cone of light can be decreased gradually, whereupon the red margin on the left becomes orange-red and this color in turn passes into the yellow tint of the strongly illuminated field ; at the same time the blue of the right margin passes into green and thence into the yellow hue of the field.

Similar phenomena, though less brilliant, are visible at the indistinct shadow edges produced in the field by placing the finger below the condenser (method 3 above, daylight illumination) or by using the sliding stop in the lower focal plane of the condenser (method 2 above). The red and blue fringes described above appear and their explanation is similar to that given for the fringes observed with the Nernst glower. The angle between the incident rays which enter the semi-dark edge is in all cases sufficiently small to allow minute angular differences between the slightly dispersed colored rays to be detected. The greater the difference in dispersion between liquid and mineral grain, the more brilliant and purer the red and blue margins thus obtained. With high-power objectives the semi-dark shadow zone covers the entire field and the colors are spread out and correspondingly less distinct and brilliant. For this reason high-power objectives are as a rule less favorable than low objectives for the determination of relative refractive indices by this method of oblique illumination.

A remarkable display of these colored margins resulting from prismatic color dispersion can be seen on a clear quartz crystal immersed in a mixture of clove oil with a little cinnamon oil and illuminated by oblique rays entering the glass base of the containing receptacle (beaker glass or trough of axial angle apparatus). Attention was first directed to these phenomena by O. Maschke in 1872.*

The color fringes as ordinarily obtained are rarely pure red and blue but rather orange and pale blue, the blue being often more pronounced than the orange. In case the liquid has a very strong dispersion and the mineral a weak dispersion, such color-rims appear over a considerable range of refractive indices and the refractive index values obtained by the method are correspondingly less accurate. Ordinarily, when colored rims are observed on a mineral grain and both sides present about the same intensity of illumination, the refractive index of liquid and mineral are equal for a wave length of about $550\mu\mu$ and the error of the determination of the refractive index by

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* Pogg. Ann., cxlv, 568, 1872 ; Wied. Ann., xi, 722, 1880.

this method is then not over ±·002; but as noted above, this probable error is noticeably larger when strongly dispersive liquids, such as methylene iodide, are used. For more accurate work recourse should be had to monochromatic light where differences of ±·001 in refractive index can be readily detected either by the oblique illumination or by the Becke line method on clear grains* measuring at least ·001^{mm} in diameter.

In view of the ease with which this method can be applied to the determination of relative refractive indices of minerals both in thin sections of rocks and in grains immersed in liquids, it is surprising that it is not more frequently used by petrologists. For the detection of small amounts of orthoclase in a rock in which plagioclase is the predominating feldspar, the writer has found oblique illumination (by method 3 above) with a relative low power objective exceedingly useful. The low refracting grains of orthoclase appear to stand out in relief (as hollows) in the slide and can be detected at a glance, whereas if the usual Becke line test be applied with a higher power objective to individual grains, the chances are that the minute orthoclase grains will be overlooked and missed altogether. In the first case it is like finding a needle in a haystack; in the second, like finding the same needle when it reflects the sun's rays which the observer cannot fail to see.

A simple field method for distinguishing calcite and dolomite.

To one accustomed to the above immersion method for determining the refractive indices of mineral grains the following method for distinguishing calcite and dolomite in the

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* For a description of a set of suitable refractive liquids see Journal Geology, xx, 494, 1912; also Carnegie Institution of Washington Pub. 158, in which the practical working details of this and other methods are given. Attention may here be directed to a method described by Anton Pauly (Zeitschr. Wiss. Mikroskop., xxii, 344-348, 1905) for measuring the refractive index of a liquid by means of sections of calcite and siderite cut parallel with the axis. From the angle 2ϕ between the two positions at which the mineral plate disappears in the liquid, Pauly calculates the refractive index of the liquid from the equation

$$n = \sqrt{\frac{\omega e}{\epsilon^2 \sin^2 \phi + \omega^2 \cos^2 \phi}}$$

where ω and ϵ are the principal refractive indices of the mineral. Pauly claims an accuracy of 2 or 3 in the fourth decimal place for this method. His fundamantal assumption, however, that the mineral plate actually disappears, is incorrect. For every position of the plate two waves emerge, one vibrating parallel to ω and the other parallel to ϵ. The intensity of the wave ω varies with $\cos^2 \phi$, where ϕ is the angle included between ω and the principal section of the polarizer; the intensity of the second wave ϵ varies with $\sin^2 \phi$. Two waves emerge and, except for $\phi = 45°$ their intensity is different. There is consequently no position where the plate disappears entirely (i. e., has the same refractive index as the liquid), and the method cannot furnish accurate results.

field may prove useful. The ordinary refractive index, ω, of calcite is 1·658; that of dolomite, 1·682. Grains of calcite immersed in a-monobrom-naphthalene ($\omega = 1{\cdot}658$) show distinct color fringes; such color fringes do not appear along the margins of dolomite grains. To apply the method in the field two object glasses and a small bottle of a-monobrom-naphthalene* are necessary. The material to be tested is finely powdered with the hammer and a small portion immersed in a drop of the a-monobrom-naphthalene on the object glass. The drop and immersed powder are then covered with the second object glass and the whole tilted and examined through a pocket lens pointed toward the sky. Oblique illumination is procured by placing the finger in front of the object glass (between the glass and the sky). The edge of the finger then appears out of focus and indistinct; grains of calcite within this semi-dark zone of indistinct focus show the characteristic blue and orange marginal colors, while grains of dolomite appear simply white and dark. Here and there a suggestion of color is to be observed even with the dolomite, but with a little practice the eye becomes accustomed to these differences and the two substances can be readily distinguished by this method. The writer has had occasion to use the method repeatedly during the past decade.

The phenomena of convergent polarized light observed in parallel polarized light.

By the use of oblique illumination practically all of the phenomena which are obtained in convergent polarized light can be obtained without difficulty. The importance of oblique illumination in this respect has been emphasized by Schroeder van der Kolk,† v. Fedorow,‡ and recently by Schneiderhöhn.§ Schroeder van der Kolk obtained oblique illumination (1) by use of a stop above the condenser (method 4 above); (2) by casting a shadow with his finger placed between the reflector and the source of light (modification of method 3 above); (3) by tilting the plate mounted on the top surface of a glass hemisphere. Fedorow used the universal stage for the same purpose. Schneiderhöhn recommends a stop (Schieberblende) in the eye circle of the ocular. From the discussion in the first section of this paper it is evident that the most effective method for obtaining oblique illumination is by methods 2 and 3 above, unless accessory apparatus, as a glass hemisphere or a universal stage, is to be used.

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*Readily obtainable from dealers in chemical supplies.

† Zeitschr. Wiss. Mikros., viii, 456–458, 1892; xii, 188–192, 1895.

‡ Zeitschr. Kryst., xxiv, 603–605, 1895.

§ Ibid., l, 231–241, 1912.

By observing the rise and fall of interference colors on a mineral plate for light waves incident under different angles and in different azimuths, it is possible to determine the crystal system of the mineral, as Schroeder van der Kolk and Fedorow were the first to show. It should be noted, however, that the results obtained by this method of observation are also obtainable from interference figures in convergent polarized light. This can be clearly demonstrated by means of a small movable stop in the lower focal plane of the condenser (method 2 above); by shifting this stop, light from any point in the field can be had to the exclusion of all other rays and thus any particular interference color in the interference figure singled out for observation. If now, without disturbing the stop, the mineral plate itself be observed, its interference color will be found to be identical with that noted in the interference figure. By moving the stop to different positions, different interference tints can be obtained, but in all cases the interference color observed through the stop in the interference color is identical with that observed on the plate itself. The reason for this relation is not far to seek. The lower focal plane of the condenser is conjugate to the upper focal plane of the objective while the object plane is conjugate to the image plane in the eye-piece. The interference phenomena take place in the upper nicol and the interference colors as we observe them appear after the waves have emerged from the upper nicol; after the interference color has been once formed it does not suffer further change except for the errors of the lens system. It is evident, therefore, that the interference color produced by a narrow beam of obliquely transmitted light is practically the same, whether seen in the interference figure or on the mineral plate itself.

An excellent illustration of this phenomena can be had by observing a basal section of a uniaxial mineral. In convergent polarized light such a plate furnishes a black cross with concentric isochromatic lines. If a stop with small opening be used and only a narrow cone of light be allowed to pass through the plate parallel to its principal axis (the central part of the interference figure), the plate itself will appear much darker than it does when a wider cone of light is employed. By shifting the stop in one of the diametrical planes parallel with the principal nicol planes (i. e. parallel with one of the dark bars in the uniaxial interference figure) the field preserves its darkness; but if the stop be shifted along a diagonal diametral plane so that in the interference figure the small aperture appears in the light quadrants between the dark bars, the plate itself becomes noticeably illuminated, thus giving rise to the dull gray interference tints characteristic of most sections of uniaxial minerals cut normal to the principal axis. This interrelation of the phenomena observed on plates in obliquely incident, plane-polarized light and those seen in interference figures from the same plates in convergent-polarized light is fundamental but has not always been appreciated by observers.

Recently H. Schneiderhöhn* has elaborated this method of oblique illumination and employed a stop in the eye circle of the ocular for the purpose (method 7 above); this position is, however, not the best for ordinary work, because of the comparatively small eye circle, and the small angle of emergence of the transmitted rays (8° to 15°) and also for the reasons cited above under methods 6 and 7. The special advantage claimed by Schneiderhöhn for this method, that it produces narrower rims of total reflection on mineral grains than are obtained by any of the substage methods, is of little practical moment and is more than outweighed by its unfavorable features. Schneiderhöhn does not recognize, moreover, the connection between the interference colors obtained on a plate in obliquely incident, parallel, polarized light and those observed in the interference figure, and is thus led to make several incorrect statements. Thus the assertion that on a section perpendicular to the optic normal, the interference colors for all obliquely incident waves are lower than that of the central wave,† is not correct, as can be shown both by direct test in convergent polarized light, and also by mathematical reasoning. Sections of all uniaxial minerals parallel with the principal axis and of biaxial minerals parallel with the plane of the optic axes exhibit in convergent polarized light the well known fall of interference colors in the direction of the acute bisectrix but rise of interference colors in the adjacent quadrants.

FIG. 18*a*.

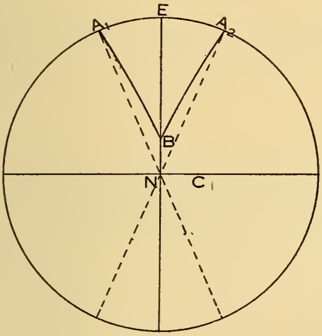
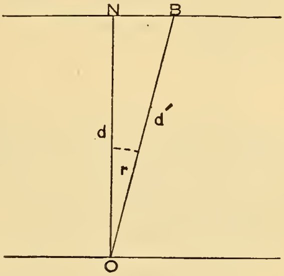


FIG. 18*b*.



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* Zeitschr. Kryst., 1, 231–241, 1912.

† Ibid., 1, 237, 1912.

In minerals with large optic axial angle (2V nearly 90° as in olivine) the rise and fall of the interference colors away from the center of the field is so slight that practically the same interference color covers the entire field and one is at a loss to determine, by this method, which quadrant contains the acute bisectrix.

The mathematical proof of the above statement is not difficult. In fig. 18*a* let N be the direction of the optic normal in stereographic projection ; A_1, A_2 be the two optic axes, and B the direction of propagation of a wave transmitted obliquely through the plate perpendicular to the optic normal N. If d be the thickness of the plate, then the length d' (fig. 18*b*) of the path of the wave OB is

$$d' = \frac{d}{\cos r} \qquad (1)$$

where r = NOB. The birefringence $\gamma' - \alpha'$ for the direction B is readily found from the standard approximate birefringence formula

$$\gamma' - \alpha' = (\gamma - \alpha) \sin \theta_1 \,.\, \sin \theta_2 \qquad (2)$$

wherein θ_1 and θ_2 are the angles BA_1 and BA_2 included by the direction B with the two optic axes A_1, A_2 respectively. In this particular case $\theta_1 = \sphericalangle BOA_1 = \sphericalangle BOA_2 = \theta_2$. In the spherical triangle BEA_1 we have

$$\begin{aligned} \cos BA_1 &= \cos BE \,.\, \cos EA_1 \text{ or} \\ \cos \theta_1 &= \cos (90 - r) \cos V \end{aligned} \qquad (3)$$

where $EA_1 = V$, which is half the optic axial angle A_1A_2.

The path difference Δ_B or interference color of the wave propagated along OB varies directly with the length of path OB (d') and the birefringence, $\gamma' - \alpha'$.

$$\Delta_B = d' \,.\, (\gamma' - \alpha') \qquad (4)$$

On substituting in this equation the value from (1), (2), (3), we find

$$\Delta_B = \frac{d}{\cos r} (\gamma - \alpha) (1 - \sin^2 r \,.\, \cos^2 V) \qquad (5)$$

The path difference Δ_N for the optic normal ON is

$$\Delta_N = d \,.\, (\gamma - \alpha) \qquad (6)$$

From (5) and (6) we obtain by division

$$\frac{\Delta_B}{\Delta_N} = \frac{1 - \sin^2 r \cos^2 V}{\cos r} \qquad (7)$$

Similarly for the direction OC (NC = NB) in the plane of the obtuse bisectrix we find

$$\frac{\Delta_C}{\Delta_N} = \frac{1 - \sin^2 r \sin^2 V}{\cos r} \qquad (8)$$

From the last two equations it is evident that for $V = 45°$, the path difference in the two quadrants at B and C is the same. For the small angles $r\,(< 20°)$ which enter into the problem we may write without appreciable error

$$\frac{\Delta_B}{\Delta_N} = \frac{1 - r^2 \sin^2 V}{1 - \frac{r^2}{2}}$$

an expression which becomes, for $V = 45°$

$$\frac{\Delta_B}{\Delta_N} = \frac{1 - \frac{r_2}{2}}{1 - \frac{r_2}{2}} = 1$$

For the direction OB the path difference is identical with that for ON when the optic axial angle is exactly 90°. The same relation obviously holds true for the direction OC. In other words, the interference color remains unchanged and covers the entire field. If now V decreases, equation (7) obviously becomes less than unity while equation (8) increases in value and is greater than unity. The interference color falls, therefore, in the direction of the acute bisectrix and rises in the direction of the obtuse bisectrix except for the case $2V = 90°$, where the interference color remains unchanged and the entire field appears isochromatically illuminated.—Both experiment and theory thus disprove Schneiderhöhn's statement. His rule,* furthermore, for distinguishing sections perpendicular to the optic normal from sections perpendicular to the obtuse bisectrix by noting that, in the first case, the interference colors fall in all directions, while in the second they fall in one quadrant and rise in the adjacent quadrant, is likewise invalid. Equally incorrect is the assertion that the eye circle stop (Schieberblende) furnishes results which cannot be obtained from the interference figure.

Recapitulation.—The study of interference phenomena resulting from oblique illumination between crossed nicols enables the observer to determine many optical features in a given mineral plate. These phenomena are identical, so far as interference colors go, with the phenomena obtained in

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*Zeitschr. Kryst., 1, 240, 1912.

interference figures from the same plate in convergent polarized light. The study of mineral plates by the method of oblique illumination is of value because it impresses the mind of the observer with the interdependence of optical and crystallographic properties. It is, however, highly important that the observer realize the essential agreement between the phenomena observed in oblique illumination and those seen on interference figures in convergent polarized light. In the interference figures the interference color phenomena are seen at a glance, and if they be studied with reference to the position of the mineral from which they are obtained, all of the conclusions to be ascertained by means of the method of oblique illumination can also be derived with even greater facility from the interference figure. For the study of interference phenomena the method of oblique illumination does not offer any special advantages over the convergent polarized light method, but it does present certain disadvantages in manipulation and in the distinctness of the phenomena observed which cannot be disregarded entirely. This is especially true if oblique illumination be obtained by use of a stop in the eye circle of the ocular as recently suggested by Schneiderhöhn. The best method for obtaining oblique illumination is that outlined under method 2 above.

Measurement of Extinction Angles.

In the foregoing pages the phenomena produced by oblique illumination have been discussed in some detail. Attention should also be directed to an obvious but important fact, too often disregarded in petrographic microscope work, that for the accurate measurement of extinction angle central illumination by parallel plane-polarized light is highly essential. Satisfactory measurements of extinction angles cannot be made when the section is illuminated by a strongly convergent cone of light, incident under all angles and in all azimuths. The reason for this is apparent from the discussion above and requires no further comment.

Geophysical Laboratory,
Washington, D. C.,
October, 1912.

ART. IX.—*Notes on the Silurian Limestone of Milesburg Gap, near Bellefonte, Pennsylvania;* by THOMAS C. BROWN.

IN the central part of Center county from Bellefonte northwest through Milesburg and on toward Snowshoe is exposed, within a distance of about ten miles, one of the most complete and most accessible sections of Paleozoic rocks which can be found anywhere in the State of Pennsylvania. It includes all of the formations represented here from the base of the Beekmantown (Lower Ordovician) to the coal measures of the Pennsylvanian (Upper Carboniferous). The lower part of this section, consisting of the various members of the Ordovician, has frequently been described and alluded to because it is one of the most complete sections of this system which can be found in the eastern part of North America. The object of this paper, however, is to record a few observations on the limestone beds which occur at the top of the next higher (Silurian) system, and to correct a few errors which have crept into the scanty descriptions of this region already in print.

The region lies at the boundary between the last fold or anticline of the Appalachian mountains and the front of the Allegheny plateau. All formations in this vicinity outcrop in a general north-east-southwest direction, parallel to the major physical features. Nittany valley occupies the last eroded anticline along the northwest side of the Appalachian mountains; the Bald Eagle ridge with its double crest is due to the resistant, almost vertical beds of the Bald Eagle conglomerate and Tuscarora sandstone on either side with the soft, easily weathered Juniata red shale between them. These beds form a part of the steeply dipping northwest limb of the Nittany valley anticline. Between the Bald Eagle ridge and the Allegheny front is the long narrow Bald Eagle valley underlain by Silurian and Devonian rocks.

The Silurian beds are well exposed along the railroad track from Milesburg gap, about one mile north of Bellefonte, almost to the railroad bridge across Bald Eagle creek at Central City. This bridge rests upon typical Oriskany sandstone containing the characteristic Oriskany fossils in great abundance. The northwest slope of Bald Eagle ridge is underlain by a shale which has generally been referred to the Clinton. Between this horizon and the Oriskany sandstone come two distinct limestone beds separated by a considerable thickness of shale. These two limestones are the subject of the present discussion.

This section was described by Rogers in 1858 and he gave a cross section to illustrate the structure of the region (fig. 1A). This is his description :*

"The next exposure of the Scalent (cement) and Pre-meridian limestones is at the Old Eagle Furnace, 200 yards up the unusually long and gentle ascent of the mountain. On the west side of the gap, the limestone strata are seen dipping 45° W. 70° N.

"They appear again in vertical layers on the summit of the short hill opposite the foot of the mountain, and again, dipping 30° N. 30° W., in the face of the next little ridge at the north foot of which flows the creek. Thus we have a synclinal aand an anticlinal flexure, in the former of which, 100 yards north of the foot of the mountain, is a little patch of the Cadent black slate, the sole relic of that formation. The Meridian sandstone lies in fragments, with great deposits of sand, on the south slope of the first, and forms the crest of the second little ridge.

"The Pre-meridian or upper division of the limestone is filled with curved and delicately formed corals, visible only on weathered surfaces."

FIG. 1.

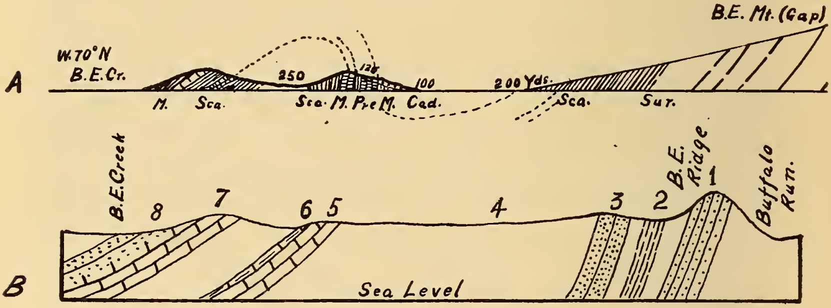

FIG. 1–A. Copied from Rogers' "Fig. III,—Section at Eagle Furnace, Bald Eagle Creek Valley," in the Final Report of the First Geological Survey of Pennsylvania, p. 546. This section is along the line A–B, fig. 3.

FIG. 1–B. A section along the line C–D, Fig. 3, Scale : 3″ = 1 mile. 1, Bald Eagle conglomerate ; 2, Juniata red shale ; 3, Tuscarora sandstone ; 4, ? Clinton ; 5, Decker Ferry ; 6, Roudout ; 7, Oriskany (limestone phase) ; 8, Oriskany sandstone.

In 1884, d'Invilliers in "The Geology of Centre County" quotes Rogers' description of these limestones and correlates Rogers' Pre-meridian with the Lower Helderberg or Lewistown limestone, No. VI of the Second Geological Survey of Penn-

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* H. D. Rogers, Final Report, Geol. Sur. of Pa., vol. i, p. 546.

sylvania. He includes in this No. VI, both the Scalent (cement) beds and the Pre-meridian of Rogers as is clearly indicated on his cross section, although he does not definitely make that statement. He apparently failed to find the anticline and syncline in these beds described by Rogers, for in mapping the limestone, No. VI, he makes it one continuous band with a slight bend in the outcrop south of Milesburg (fig. 2). He makes these further observations :*

Fig. 2.

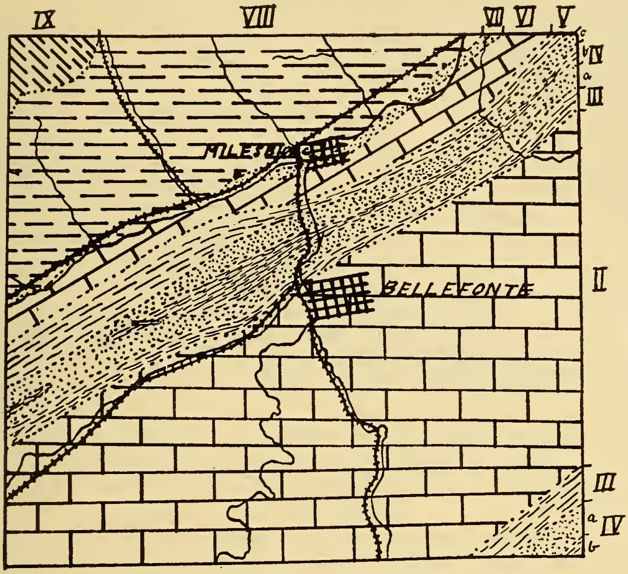

Fig. 2. Geological map of the Milesburg region copied from d'Invilliers report on the Geology of Centre County. II, Lower Silurian (Ordovician Limestones ; III, Hudson River and Utica slates ; IVa, Oneida sandstone ; IVb, Medina Red sandstone ; IVc, Medina White sandstone ; V, Clinton Red shale ; VI, Lower Helderberg limestone ; VII, Oriskany sandstone ; VIII, Marcellus, Hamilton, Genesee, Portage, Chemung ; IX, Red Catskill.

"Bald Eagle mountain west of Milesburg shows quite a decided terrace about half way up its north flank. It must be made by the limestone of VI as the Clinton No. V rides high up the mountain, even forming its crest for a short distance west of Spring creek. In the gap the dip of the measures varies from 50°–80° to the northwest, and averages about 70°."

He gives the following description of the outcrop which Rogers made the eastern limb of his syncline :†

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* Second Geol. Sur. Pa., Report of Progress, vol. T4, p. 281.

† Ibid., p. 281.

"The opening in the Lower Helderberg limestone referred to by Prof. Rogers is evidently at Swoyer's quarry. The limestone dips from 30°–40° N.W., showing a slip or crimple on the north side with the edges turned up and dipping S.E. 10°. The limestone is sparingly burned, and occurs in thin layers 2–3 feet thick, intercalated with bands of gray argillaceous shale, and under a cover of 8′ of sandy soil derived from the mountain."

Fig. 3.

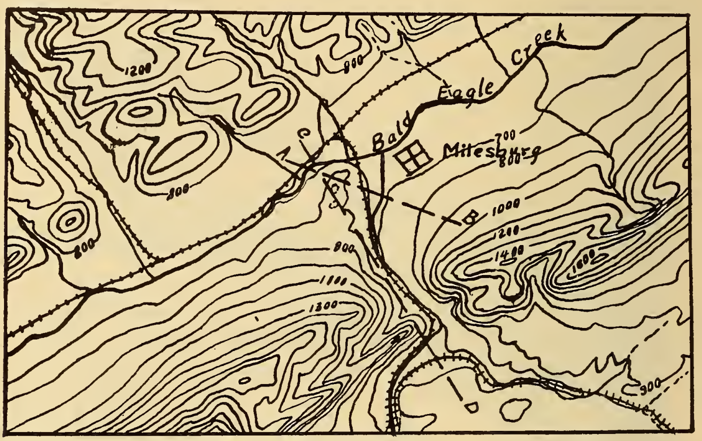

Fig. 3. Sketch map of the Milesburg region traced from the U. S. G. S. map of the Bellefonte Quadrangle. Hundred foot contours only are shown.

The outcrop on the opposite (west) side of Spring creek he describes thus:*

"This rock makes quite a decided ridge and is again opened on west side of Spring creek. In the opening the rock seems devoid of fossils, is thin and siliceous, and beds for burning must be selected with care. The whole formation, measured by outcrop, is something like 1000′ thick, though generally so covered as to make careful measurements impossible. Bald Eagle creek at Milesburg shows Oriskany s.s. No. VII outcropping in plates on south side beneath the Bellefonte R.R. bridge."

From this description it is quite evident that d'Invilliers included under No. VI (Lower Helderberg limestone) all of the beds between the so-called Clinton shale and the typical sandstone of the Oriskany. In an appendix to the volume quoted above (pp. 429–430) are a few notes on these beds by A. L. Ewing of State College. He gives the following list of fossils from the formation but does not say at what locality or in what part of the beds they were found: *Atrypa reticularis*,

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* Ibid., pp. 281–282.

Strophomena rugosa, *Spirifer perlamellosa* (?), *Trematospira* (?), *Zaphrentis*, Corals.

In 1892, J. P. Lesley in the final report of the survey referred to this region, quoting from d'Invilliers and Ewing the observations given above. This seems to be the latest published description of the region.*

The author's attention was first attracted to these beds when Dr. E. S. Moore, of State College, called upon him to help identify a small collection of fossils from these limestones. At once it became apparent that there was considerable confusion in the terms applied to these beds and some error in their interpretation. A study of the fossils above mentioned was supplemented by visits to outcrops in the field, where a considerable collection of fossils was made and the outcrops carefully studied.

The beds referred to by d'Invilliers as No. VI, or Lower Helderberg, in reality contain representatives of more than one horizon, the lower part being equivalent to the Decker Ferry of northeastern Pennsylvania and New Jersey and the upper part containing a typical Oriskany fauna, which is identical with that found in the sandstone above.

The lowest distinct limestone bed which outcrops on the first little ridge north of the gap and southwest of Milesburg (fig. 1–B, bed 5) yielded a good fauna, although largely composed of corals, in which the following species have been identified.

Diphyphyllum integumentum Barrett.
Cladopora rectilineata Simpson.
Cladopora bifurcata Grabau.
Favosites pyriforme Hall.
Favosites corrugatus Weller.
Halysites Catenularia (Linn).
Proetus pachydermatus Barrett.
Proetus spinosa Weller.

In addition to these there were several Cyathophyllum-like or Zaphrentis-like corals which have not yet been identified. Several of these show carinæ and may be identical with those described by Grabau from the Monroe beds of Michigan.

Of the above mentioned species *Cladopora rectilineata* is by far the most abundant, and is no doubt the form referred to by Rogers when he said that: "The Pre-meridian or upper division of the limestone is filled with curved and delicately formed corals, visible only on weathered surfaces." Along the crest of this limestone ridge certain thin beds are composed almost wholly of this coral. Brachiopods are sparingly represented here although no specimens were obtained in such condition that they could be identified.

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* Summary Final Report, vol. ii, p. 1002.

This limestone has been opened up at a number of places along the ridge. Possibly some of these openings may have been newly made when Rogers visited this region over fifty years ago. At present they are concealed by a timber growth and many of the trees growing in the quarry openings are at least thirty years old and possibly much older.

In one of these old openings high up on the hillside near the end of the ridge, the limestone was observed passing upward into a more shaly bed. From the weathered portions of this shaly limestone a very rich ostracod fauna was obtained. In addition to the ostracods only a single brachiopod and one coral were found at this horizon. The following is a list of the species identified :

Cyathophyllum hydraulicum (Simpson).
Whitfieldella nucleolata (Hall).
Leperditia alta (Conrad).
Leperditia Altoides Weller.
Leperditia elongata Weller.
Leperditia gigantea Weller.
Leperditia jonesi Hall.

The strata overlying this shaly limestone bed are apparently shales, for they have weathered down to form the slight depression between this and the next limestone ridge. No outcrop of these strata was observed.

The next limestone ridge is also fossiliferous both where it is exposed at the railroad track and higher up on the hill side. No extensive collection was attempted at this horizon but numerous specimens were found and every one that could be identified was an Oriskany type, such as is found here in the overlying white or yellow sandstone as well as in the Oriskany of New York. The most abundant species were these: *Spirifer murchsioni*, *Leptocoelia flabellites*, *Rensselaeria ovoides*, *Platyceras nodosus*. It is evident then, that this upper limestone is a part of the Oriskany.

From the list of fossils given above it is also evident that the lower limestone is much older and should be correlated with the Decker Ferry while the overlying shaly bed contains a fauna typical of the Rondout of New Jersey and eastern New York.

The object of this paper is twofold: first to show clearly what the structure of this region is, and second, to definitely place in the geological column the limestones which have been mentioned. The accompanying diagram (fig. 1-B) will show what the structure is, and when compared with Rogers' figure (fig. 1-A) it can easily be seen where he was in error. The lists of fossils given above show that the lower limestone horizon can be correlated with the Decker Ferry of New Jersey and the division between this and the overlying shaly limestone is the dividing line between the Decker Ferry and the Rondout. No attempt is made to discuss the shale beds lying above these limestones and below the Oriskany. Likewise, no attempt is made to discuss the so-called Clinton shales lying beneath this Decker Ferry horizon. However, it is the conviction of the author that these beds are not of Clinton age, but rather will eventually be found to correlate with the Poxino Island shale and Bossardville limestone of the New Jersey section and their equivalents in New York. No attempt has been made to correlate any of the beds above mentioned with the beds of probably corresponding age which outcrop along the west bank of the Susquehanna in Perry county. It seems to the author that these Perry county beds should be thoroughly restudied along the lines of the more recent work in New Jersey and New York before any such attempt is made.

Art. X.—*On a Cerussite Twin from the Mammoth Mine, Pinal County, Arizona*;* by Joseph E. Pogue.

The specimen under consideration (Catalogue No. 86362) came into the possession of the United States National Museum in 1908 with the acquisition of the Hambach Collection of fossils and minerals. It was labelled "Mammoth Mine, Arizona"; no further information is available concerning its occurrence.

Fig. 1a.

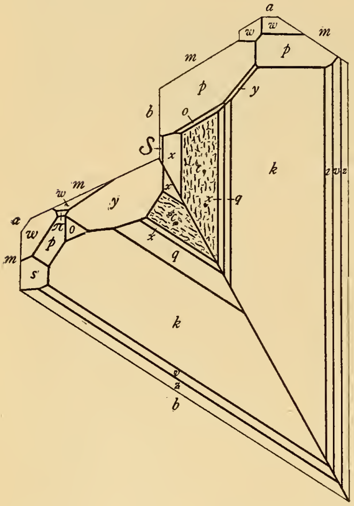

Fig. 1b.

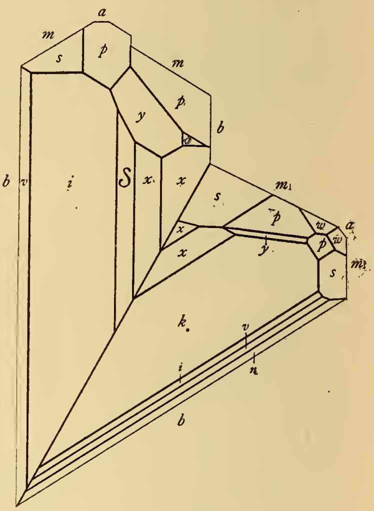

Fig. 1a. Top view of cerussite twin. Projection on base, $c = 0\ \{001\}$.
Fig. 1b. Bottom view of same. Projection on base, $c = 0\ \{001\}$

Description.—Colorless, transparent. Dimensions $10 \times 10 \times 7^{mm}$. Faces sharp and suitable for measurement.† Contact twin, the two individuals nearly equally developed. Fig. 1*a* shows the crystal as viewed from above, projected upon the base $c = 0\ \{001\}$; fig. 1*b* represents the under development of the same crystal, projected also upon the base. In fig. 2 is given a gnomonic projection of the upper half of the crystal (as represented in fig. 1*a*), which shows clearly the relation of the two individuals.

* Published by permission of the Secretary of the Smithsonian Institution.

† The measurements were made on the two-circle goniometer in the mineralogical laboratory of Prof. V. Goldschmidt in Heidelberg.

Forms.—The forms identified are listed in the following table:

Letter	:	c	b	a	m	(r)	x	q	k	S
Symbol Gdt.	:	0	0∞	∞0	∞	∞3	$0\frac{1}{2}$	$0\frac{2}{3}$	01	$0\frac{3}{2}$
—— Miller	:	001	010	100	110	130	012	023	011	032

Letter	:	i	v	z	n	y	π	p	o	w
Symbol Gdt.	:	02	03	04	05	$\frac{1}{2}0$	$\frac{3}{2}0$	1	$\frac{1}{2}$	21
—— Miller	:	021	031	041	051	102	302	111	112	211

Fig. 2.

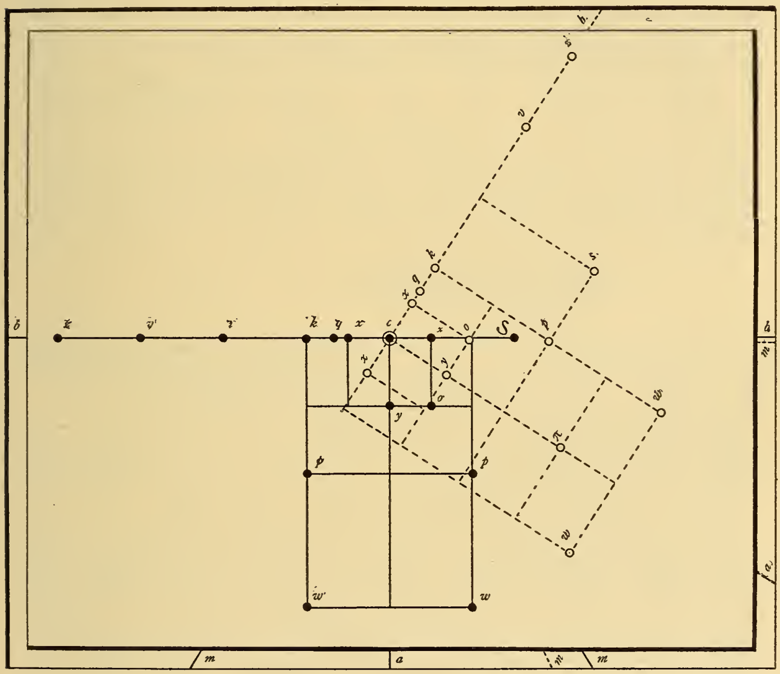

Fig. 2. Gnomonic projection of upper portion of cerussite twin.

Of these all are common, with the exception of q, S and π, which have been noted on less than 1 1/2 per cent of the several hundred cerussite crystals thus far examined crystallographically. π for the first time is found present on a twin after the r-law. r appears only as the twinning plane uniting the two individuals. The basal planes, as shown in fig. 1a, are pitted by natural etching. The combination of forms is the richest yet noted for a twin of this type.

Twinning.—Cerussite exhibits two twinning laws: (1) the m-law, in which the common prism $m = \infty$ $\{110\}$, or a plane at right angles to it, is the composition plane; and (2) the *r*-law, whereby the two individuals are united by the prism $r = \infty 3$ $\{130\}$. The first law is more common than the second, because the *m*-prism is potentially stronger than the *r*-prism, as shown by its presence in the important zone *c p m*[*] and its more frequent occurrence on crystals. In a tabulation[†] made in 1904 of all the combinations thus far noted on cerussite, the *m*-law was represented on 90, and the *r*-law on 27, out of a total of 398 crystals listed.

The present specimen is twinned after the *r*-law; the angle between the two individuals, as shown both in the basal and gnomonic projection, is 57° 18′. Twins of this type, first noted in 1870 by Koksharow[‡] from the Altai Mountains in Siberia, are now known from about 18 foreign localities and 4 sources in North America. The latter include, in addition to the locality afforded by the present example, the Begoña Mine, Cerro de San Pedro, San Luis Potosi, Mexico;[§] the Red Cloud Mine, Yuma County, Arizona[‖] (yielding specimens similar in habit, though poorer in forms than the one here described); and Granby, Missouri.[¶]

Division of Mineralogy and Petrology,
United States National Museum,
Washington, D. C.

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[*] For a clear exposition of the theory of twinning, illustrated by cerussite, consult Goldschmidt, Neues Jahrb. für Min., Beilage-Band, vol. xv, 1902, pp. 562–593. The *r*-law of twinning in cerussite is discussed on p. 582.

[†] Hubrecht, Zeitschr. für Kryst., vol. xl, pp. 179–185, 1904–05.

[‡] Mat. Min. Russlands, vol. vi, p. 111, 1870.

[§] Hunt and Van Horn, this Journal, vol. xxxii, p. 45, 1911; Zeitschr. für Kryst., vol. xlix, p. 357, 1911.

[‖] Pirsson, this Journal, vol. xlii, p. 405, 1891.

[¶] Pirsson and Wells, this Journal, vol. xlviii, p. 219, 1894.

Williams (Johns Hopkins Univ. Circ., No. 87, April, 1891, p. 74) is cited by Hunt and Van Horn (loc. cit.) as well as by Dana (System, 1892, p. 1030) as describing cerussite twinned after the *r*-law from the Mountain View Mine, Carroll County, Maryland. The writer has examined the original publication and finds that of two twins described, the second follows the *m*-law, and the first, while figured, is not sufficiently characterized to afford definite recognition of its twinning plane, though the writer judges it also to be *m*.

Art. XI.—*The Preparation of Selenic Acid and Sodium Selenate for Use as Reagents in the Determination of Bromine in Haloid Salts*; by Philip Lee Blumenthal.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxxxix]

Selenic acid and sodium selenate have been proposed in a previous paper from this laboratory* as reagents for the qualitative elimination of bromine, in determinable form, from haloid salts. These reagents when made by ordinary methods† may contain contaminating material likely to be objectionable. The following methods have therefore been devised for the preparation of these reagents in such condition that any foreign material remaining in them shall not interfere with the success of the analytical process.

Selenic Acid.

The method proposed for the preparation of selenic acid depends upon the action of nitric acid and potassium bromate upon selenious acid, the bromic acid formed reacting with the selenious acid according to the following equation:

$$3H_2SeO_3 + HBrO_3 = 3H_2SeO_4 + HBr.$$

Further action of the bromic acid breaks up the hydrobromic acid, according to the equation

$$HBrO_3 + 5HBr = 3Br_2 + 3H_2O.$$

Upon evaporating the solution to low volume, a second liberation of bromine accompanied by nitrogen oxides takes place, apparently according to a reaction like the following:

$$2HBrO_3 + 2HNO_3 = 2H_2O + Br_2 + 2NO_2.$$

The free bromine and the nitrogen oxides are, of course, easily volatilized. The preparation of selenic acid based upon these reactions was put to the test as follows:

Preliminary Test.—Selenious acid was prepared by dissolving elementary selenium in nitric acid and evaporating the solution to dryness. The crude selenious acid so obtained was sublimed from manganese dioxide according to the method used by Norton,‡ and the thin needle-like crystals were bottled as rapidly as possible. A solution convenient for use was made by dissolving 2 grm. of the purified selenium dioxide in 200^{cm^3} of water and a portion of 20^{cm^3}, containing 0·1 grm. of the dioxide, was used for each test. To each portion, contained in an Erlenmeyer flask, were added 10^{cm^3} of 1·1 nitric acid and a little potassium bromate, and this solution was evaporated to a low volume. When barium

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* Gooch and Blumenthal, xxxv, 54.

† Gmelin-Kraut, Handbook, Anorg. Chem., i, 769, 1907.

‡ This Journal (4), vii, 290.

nitrate was added to the concentrated solution, and the free acid nearly neutralized with ammonium hydroxide, white barium selenate was precipitated. Though impure on account of its tendency to occlude foreign material, this precipitate proved to be practically free from selenious acid.

Preparation of the Reagent.—To 10 grm. of selenium dioxide dissolved in 75^{cm^3} to 100^{cm^3} of water were added 6 grm. of potassium bromate and 4^{cm^3} of strong nitric acid. This mixture was heated on the water bath until perfectly colorless. After the second evolution of bromine, which occurred when the volume was quite low, a little more bromate was added to decompose the excess of nitric acid and the heating was continued. When the addition of a crystal or two of bromate caused no further evolution of bromine, the colorless solution was made slightly ammoniacal, heated to the boiling point, and treated with a hot dilute solution of barium nitrate. The precipitated barium selenate, after settling, was filtered with suction, washed thoroughly with hot water, and finally transferred to a large crucible and dried at low redness. The weight of this product was about 25 grm., while the theoretical amount obtainable from the selenious acid taken was about 25·1 grams. After weighing, the selenate was treated in a porcelain crucible with 5^{cm^3} of strong sulphuric acid (sp. gr. 1·8) and some 20^{cm^3} of water. The pasty mass so obtained was heated about two and one-half hours on the water bath, and finally diluted, filtered, and washed. The filtrate and washings were made up to one liter, and an aliquot was taken for analysis by the method of Pierce.* This analysis showed about 94 per cent of the selenium taken to be present. From the determination of the selenious acid present by the method of Gooch and Clemons† it was found that 85 per cent of the selenium was present as selenic acid, the presence of selenious acid in the final product being due in this case to the fact that the barium precipitation was made in alkaline solution, under which conditions barium selenite is also precipitated. The total yield of selenic acid was 78 per cent of the theoretical. Later experiments have shown that the contamination by selenious acid may be to a large extent avoided by precipitating while the solution still contains free nitric acid.

Sodium Selenate.

The preparation of sodium selenate, to be used with sulphuric acid in place of free selenic acid, was also investigated.

Preliminary Test.—Elementary selenium (1 grm.) was fused in platinum with sodium peroxide (2 grm.) and sodium carbonate (6 grm.). The mass, after dissolving in water and filtering, barely bleached a few drops of dilute permanganate,

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* This Journal (4), i, 416.

† Ibid. (3), 1, 51.

showing that the selenium had been oxidized almost completely to selenic acid, only a little selenious acid remaining.

Next, the finely powdered metal (1 grm.) was fused with sodium peroxide (5 grm.) in a nickel crucible, and after cooling, the melt was partially neutralized with sulphuric acid, to facilitate the analysis, and filtered. The filtrate and washings were made up to 100^{cm^3} and 10^{cm^3} of this solution were analyzed by the method of Gooch and Scoville.* Two analyses showed the yield to be fairly quantitative, and suitable for the analytical elimination of bromine.

Preparation of the Reagent.—In utilizing the method on a larger scale, about 105 grm. of powdered selenium and 500 grm. of sodium peroxide were thoroughly mixed and fused in charges containing 10 grms. to 15 grms. of selenium, nickel crucibles being employed. The reaction was rapid and a few minutes' heating over a Bunsen burner sufficed to bring the mass to liquid condition. After cooling, the crucible was placed in a beaker of cold water, and covered with a watch-glass to avoid loss by spattering. The melt dissolved with great evolution of heat, and cold water was added from time to time, to prevent boiling. Some finely divided material remained floating in the strongly alkaline liquid. A slight green color, probably due to the solution of small amounts of nickel, was also noticed. The solution could not be filtered through paper, and a platinum cone, lined with asbestos, was utilized, although the process was exceedingly laborious. The opaque filtrate consisted chiefly of sodium selenate and sodium hydroxide, with some sodium carbonate due to contact with the air.

In order to purify the selenate from sodium hydroxide, the attempt was first made to remove the latter by shaking the solution with alcohol. This procedure was found to have several disadvantages. The amount of time involved, the inconvenience of handling large quantities of strongly alkaline solution, and the not inconsiderable amount of carbonate formed, all militate against the process. But the greatest disadvantage lies in the fact that the dissolved carbonate and selenate of the lower aqueous layer are very difficultly crystallized. The successful method of purification ultimately developed consisted in evaporating the alkaline liquid to pasty condition over a free flame and removing as much caustic alkali as possible by continued extraction with alcohol which had been distilled from lime (97–99 per cent pure). The extraction was hastened by warming on the steam bath, but in this latter treatment, red, amorphous selenium was formed by reduction of the solution. Six or eight extractions sufficed to remove most of the hydroxide.

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* Gooch and Scoville, this Journal (3), 1, 402.

The residue, consisting chiefly of sodium selenate and sodium carbonate, could not be crystallized from water. It was found necessary to convert the carbonate to sulphate in order to obtain crystallizable material, and after careful neutralization with sulphuric acid, the mixture of sulphate and selenate was crystallized by repeated evaporations. The sulphate tends to crystallize first, and a partial separation may be accomplished in this manner. The mixed crystals of sodium selenate and sulphate first obtained were quite efflorescent, but on warming and evaporating to greater concentration, crystals of a lower order of hydration were obtained. The selenate and sulphate can also be thrown out by alcohol, but this method was not satisfactory and was discarded.

The several crops of crystals were combined, filtered on a Buchner funnel with suction, well drained, and finally the mass was heated to 108° C. for some hours, whereby most of the water was driven out, and a mixture of nearly anhydrous sodium salts was obtained. Analysis of the mixed product showed it to average about 65 per cent of selenate and the total yield of sodium selenate was about 58 per cent of the theoretical amount. Considerable material was lost in the preliminary attempts at purification, in the tests made from time to time and in the mother liquor from the crystallizations.

This material thus prepared is serviceable for immediate use with sulphuric acid in the method proposed for the separation of bromine and chlorine, and no attempts were made to separate the sulphate and selenate completely. In view of experience obtained in this work, it seems probable that by rapidly evaporating the filtered solution of selenate and hydroxide over a free flame, and rapidly extracting the residue with absolute alcohol, the carbonate formation may be, to a large degree, inhibited. This, of course, reduces the amount of sulphate ultimately formed, since the greater part of the alkali, excepting the carbonate, is removed by the alcohol treatment. The resulting aqueous solution, containing a small amount of sulphate, but no selenite, can be purified fairly well by fractional crystallization, as the selenate is more soluble in water than the sulphate.

It is to be noted that sodium selenate may also be prepared by fusing with sodium carbonate the barium selenate obtained in the process previously described for making selenic acid, the amount of carbonate taken being less than that required to decompose the barium salt completely. Upon extracting the product with water the sodium selenate dissolves and may be crystallized from the filtered solution.

The processes described afford easy means for preparing selenic acid and sodium selenate in such condition that, though these products are not pure, they are suitable for use in the quantitative elimination of bromine from haloid salts according to the methods to which reference has been made.

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *Quantitative Determination of Copper.*—For the rapid determination of copper, **Alexander Boyer** uses hydroxylamine hydrochloride in the presence of sodium hydroxide and Rochelle salt, thus precipitating cuprous oxide, which is filtered on an asbestos filter in a glass tube, washed with hot water, dried, ignited in a stream of air, and weighed as cupric oxide. With about 0·3 g. of copper in the form of sulphate, he recommends the use of a porcelain dish of about 200^{cc} capacity, the addition of 17 g. of sodium potassium tartrate and 4 g. of sodium hydroxide, both in rather strong solution, then heating to boiling and adding about 2^{cc} of a 5 per cent solution of the hydroxylamine salt, and boiling for about a minute. He shows by very satisfactory test analyses that considerable quantities of antimony, zinc, bismuth, lead, iron, arsenic, tin, ammonium, and nitrates do not interfere with the method. For analyzing alloys, such as bronze and brass, he dissolves in nitric acid, evaporates to fuming with sulphuric acid, neutralizes with sodium hydroxide, and proceeds as usual. In cases where manganese, nickel and cobalt may be present, he recommends first precipitating with hydrogen sulphide in sulphuric acid solution and then treating the resulting sulphides in the same way as the alloys. Silver interferes with the method and must be previously removed. Mercury is also precipitated, but it is driven off upon ignition.—*Zeitschr. analyt. Chem.*, li, 729. H. L W.

2. *The Dissociation of Phosphorus Vapor.*—Biltz and Victor Meyer have shown that at lower temperatures phosphorus vapor corresponds to the formula P_4 and they were able to detect dissociation at higher temperatures. Victor Meyer's method is, however, not suitable for the quantitative investigation of dissociating vapors, since the degree of dissociation is altered by the presence of an inert gas. **Stock** and **Gibson** have therefore determined the pressure temperature curves of phosphorus vapor at various volumes, using a quartz apparatus, and have found that the vapor density corresponds to P_4 up to 700° C., above which dissociation takes place according to the equation $P_4 = 2P_2$. There is no evidence of further dissociation at the temperatures investigated, and the law of mass action applied to the new measurements decides against the equation $P_4 = 4P$.—*Chem. News*, cvi, 129. H. L. W.

3. *The Contamination of Laboratory Samples by Iron Derived from Crushing Machinery.*—**Victor Lenher** has determined the amount of finely divided iron introduced into several samples of quartzite by grinding small fragments in a Braun crusher to pass a 120 mesh screen. The amount of this contamination varied

from 1·86 to 2·97 per cent in 15 samples. The metallic iron was detected by the use of a magnet, but owing to the fineness of the powder it was found to be impossible to remove all of the iron by this means, so that treatment with acid was resorted to. These results are interesting from the large amount of contamination disclosed, which is large enough to affect the results of analysis, even where iron is not considered, to the extent of 2 or 3 parts in 100. The author calls attention to the fact that great care should be used to avoid such errors in cases where grinding machines and "bucking plates" are used for pulverizing hard materials.—*Jour. Indust. and Eng. Chem.*, IV, 6. H. L. W.

4. *Volumetric Determination of Arsenic Acid.*—In connection with a study of the compounds of arsenic pentoxide with water, whereby only the previously known compounds $As_2O_5.4H_2O$ and $3As_2O_5.5H_2O$ are isolated, MENZIES and POTTER have devised a method for titrating the acid when it is pure and in the free condition. Since the acid, when neutralized, does not give sharp color changes with indicators, the authors add barium chloride to precipitate $BaHAsO_4$ during the acidimetric titration, using sodium hydroxide solution with phenol phthalein as indicator. It is necessary to use a large quantity of arsenic acid so that 30 or 40^{cc} of normal alkali, which may preferably contain some barium hydroxide, shall be used. 15^{cc} of saturated barium chloride solution are added, the liquid is diluted to 250^{cc}, boiled 15 minutes to remove carbon dioxide, cooled, and titrated with phenol phthalein as indicator. The alkaline solution is added with stirring until the locally formed precipitate begins to dissolve slowly, then the walls of the vessel under the liquid are scratched with a glass rod until the liquid appears lustrous with fine crystals, after which the titration is completed as usual. If the conditions are not adhered to, as, for example, if the liquid is too dilute, if the alkali is added too rapidly, or if the stirring is not vigorous enough, very discordant results may be obtained which sometimes approach those required for the precipitation of $Ba_3(AsO_4)_2$.—*Jour. Amer. Chem. Soc.*, xxxiv, 1457. H. L. W.

5. *Modern Inorganic Chemistry*; by J. W. MELLOR, D.Sc., 12mo, pp. 871. London, 1912 (Longmans, Green and Co. Price $2.20).—It is a pleasure to review a text-book having so many excellent features as this one. It is a large book, and its treatment of the fundamental facts and theories is unusually comprehensive. It appears to give an abundance of facts for the purpose in view with avoidance of a superfluous number of dry statements. It is written in an interesting literary style and gives many apt quotations, not only from chemical authors but also from ancient philosophers and poets, and even, in one instance, from such an authority as "Sherlock Holmes." Nothing appears to be lacking in the way of a satisfactory presentation of the most modern chemical ideas. Examination questions from all parts of the world are quoted, but it is entirely different from the books which are devised for the sole purpose of preparing for examinations. The

illustrations are good, and they include many useful graphic curves. In short, this appears to be a remarkably able and modern book, which is well suited to arouse the interest of the student.

H. L. W.

6. *A Treatise on General and Industrial Inorganic Chemistry;* by DR. ETTORE MOLINARI. Translated by DR. ERNEST FLEITMANN. Large 8vo, pp. 704. Philadelphia, 1912 (P. Blakiston's Son & Co. Price $6.00).—This English edition has been translated from the third revised and amplified Italian edition. The book is very interesting from the fact that it has been written with the novel idea of teaching the theory of chemistry in connection with an extensive treatment of the practical application of the science. The first part of the book, comprising 125 pages, is devoted strictly to theoretical chemistry, while the remaining, descriptive portion contains further theoretical discussions, but in this part special attention is given to industrial chemistry. The illustrations are numerous and good, and the book as a whole appears to be a very creditable one. H. L. W.

7. *On the Discharge between Concentric Cylinders in Gases at Low Pressures.*—In two earlier papers F. W. ASTON has given an account of his investigations upon the length of the Crookes dark space and the relation between current and potential in the discharge between large plane aluminium electrodes in different gases at various pressures. For all the chemically active gases and for the members of the helium group, when the latter were not extremely pure, it was found that the following equations hold over a rather wide range

$$D = \frac{A}{P} + \frac{B}{\sqrt{C}}, \text{(I)} \qquad V = E + \frac{F\sqrt{C}}{P}, \text{(II)}$$

D = length of dark space, P = gas pressure, V = potential difference between electrodes, and C = current density. The values of the constants A, E, and F change markedly from one gas to another, whereas B remains sensibly constant. Now, with plane electrodes in a cylindrical glass tube, the current density for points not too close to the glass walls will have the same value throughout the length of the discharge, and hence no information can be obtained as to the particular part of the discharge upon which the value of the current factor B of the dark space depends. On the other hand, if the parallel plane electrodes are replaced by two coaxial cylinders the current density will vary from point to point throughout the discharge, so that valuable information about B and the nature of the discharge in general might be expected.

Recently Aston has carried out his suggestion, using hydrogen and oxygen. The outer electrode consisted of a thin, aluminium sheet, which fitted close against the inner wall of a glass tube. The inner electrode, made of the same metal, was wound around the outside of a smaller glass tube. The electrodes were maintained coaxial by means of the insulating supports of-the smaller glass tube. The diameters of the metallic cylinders were $8{\cdot}20^{\text{cms}}$ and $1{\cdot}27^{\text{cms}}$ respectively, with a common length of $18{\cdot}0^{\text{cms}}$. No guard-ring system was employed, so that the end correction was not eliminated. However, this correction was unimportant under the experimental conditions. Details of the electrical connections and of the arrangements for varying the gas pressure will be omitted in this place. The order of an experiment was to keep the pressure constant while taking a series of readings of length of dark space and voltage for four or five definite current values, and then to change the pressure and make a new series of observations.

The general features of the discharge were the same as for plane electrodes. With oxygen the edge of the dark space was absolutely sharp at all pressures, whereas with hydrogen this edge was not nearly so well defined. When the experimental data are plotted with the lengths of the dark space as abscissæ and with the corresponding reciprocals of the square root of the current densities as ordinates, *parallel* straight lines are obtained. The "observed" points fall close to the mean lines both when the outer cylinder and when the inner one had been used as cathode. Not only is the slope coefficient B, of equation (I), constant, but it has the same value as for plane electrodes of aluminium. The only proviso is that the current in each case must be expressed as current density at the surface of the cathode. This independence of the curvature of the electrodes is particularly surprising when the fact is taken into account that the radius of curvature was of the same order as the length of the dark space, so that the current density at the edge of the negative glow must have been widely different from that at the surface of the cathode, and its distribution continually altering with the change in the length of the dark space. The equality of B for plane and cylindrical electrodes is a very important result, and it seems to indicate that, whatever may be the explanation of the shrinkage of the dark space with increase of current density, the mechanism which causes it is probably at or very near the surface of the cathode. Since B is constant, for a given gas, the observed changes in the pressure factor A lead to the conclusion that the effect of curvature of the cathode on the length of the dark space is exactly like a change in pressure, an increase if it is concave, and a decrease if it is convex. Equation (II) was also found to hold both for hydrogen and oxygen when coaxial cylinders were used as electrodes.—*Proc. Roy. Soc.*, vol. lxxxvii, No. A 597, p. 428, October, 1912. H. S. U.

8. *On the Influence of the Nature of the Cathode on the Length of the Crookes Dark Space.*—This investigation, by F. W. Aston, followed as a natural consequence of the results briefly described above. Only parallel plane electrodes in the gases hydrogen and oxygen were employed. The pairs of electrodes were made of aluminium, iron, copper, zinc, silver, tin, platinum, and lead. A few experiments were performed with

liquid cathodes and aluminium anodes, with grooved solid cathodes, and with perforated cathodes. Four parts of Aston's summary especially merit quotation. "(1) The relations between the values of pressure, voltage, current, and the length of the dark space . . . . satisfy the same form of equations as those previously given for aluminium, the constants varying considerably. (2) Roughness of the cathode surface does not appear to affect the discharge, if the dimensions of the irregularities are small compared with the length of the dark space. (3) The length of the dark space is shown, in the cases examined, to be greatest for silver and least for magnesium, the metals following the same order as in the case of the cathode fall. (4) The rate of change of length of the dark space with change of current density at the surface of the cathode seems much the same for all cathodes."— *Vide supra*, p. 437. H. S. U.

9. *Multiply-charged Atoms.*—In the photographs of positive rays previously obtained by Sir J. J. Thomson the mercury line is characterized by the exceptionally small displacement of the head of its parabola. By using gradients as high as 10,000 volts per centimeter Thomson has been able to show that the electrostatic displacement for mercury is one-eighth of the normal value for the heads of the parabola corresponding to other elements. The displacement due to the electric field is inversely proportional to the kinetic energy of the particle displaced, consequently the atoms which produce the head of the mercury parabola must have eight times the maximum amount of energy possessed by the normal atoms. This could be accounted for if some of the mercury atoms in the discharge-tube had lost eight corpuscles, for then the energy communicated to the atom by the electric field would be eight times the energy imparted to a normally charged atom. Three is the largest multiple of charge heretofore observed by Thomson, for other elements. The photograph reproduced in the paper shows seven parabolas pertaining to mercury. The eighth doubtless exists but is too faint for detection since, in general, the curves become weaker as the multiple charge increases.

A careful study of the negatives has led to the conclusion that there are two, and only two, kinds of ionization in the discharge tube. In one of these kinds the mercury atom loses 1 corpuscle, while in the other it loses 8. Moreover, there are no indications of ionization of such a sort as to deprive the mercury atom of 7, 6, 5, 4, 3, or 2 corpuscles. Positive charges between the limits 8 and 1 arise from the atom first losing 8 corpuscles in the discharge tube and subsequently regaining from 1 to 6 corpuscles respectively. Thomson's conception of the processes of ionization is stated very clearly, as follows: "In the first method the ionizing agents are the rapidly moving corpuscles which constitute the cathode rays, these very small particles penetrate into the atom and come into collision with the corpuscles inside it individually, the collision in favorable cases causing the corpuscles struck to escape from the atom; this type of ionization results in the atom losing a single charge. In the other type of ionization we suppose that the mercury atom is struck by a rapidly moving atom and not by a corpuscle ; after the collision the mercury atom starts off with a very considerable velocity, which at first is not shared by the corpuscles inside it. The tendency of the corpuscles to leave the atom depends only upon the *relative* velocity of the atom and the corpuscles inside it, so that the ionizing effect produced by the collision is the same as if the atom were at rest, and *all* the corpuscles were moving with the velocity acquired by the atom in the collision. Thus if there were eight corpuscles in the mercury atom connected with about the same firmness to the atom, the result of the atom acquiring a high velocity in a collision might be the detachment of the set of eight, leaving the atom with a charge of 8 units of positive electricity. We see in this way how the cathode particles might produce one type of ionization resulting in singly charged atoms, while the atoms forming the positive rays might produce another type of ionization resulting in multiply-charged atoms."—*Phil. Mag.*, vol. xxiv, October, 1912, p. 668.

10. *Handbuch der Spectroscopie ;*[*] by H. KAYSER. Vol. VI. Pp. vi, 1067, with 1 plate. Leipzig, 1912 (S. Hirzel).—This volume supplements the preceding one, and forms with the latter a complete unit. All the reliable wave-lengths and associated data pertaining to the elements not given in the fifth volume are collected in the sixth. As before, the alphabetical sequence is based upon the chemical symbols for the respective elements, so that sodium (Na) comes first and zircon (Zr) last. The bibliographical references have been made as complete as possible. For the first elements in the list these references close about Easter, 1911, whereas they approach July, 1912, for the last elements. The practical value of this volume is greatly increased by the presence in it of a group of special tables beginning with page 887. The first of these tables gives the wave-lengths (chiefly) of iron lines as obtained by the interferometer method alongside of the corresponding data as given by Rowland. The differences are given in the last columns and are also plotted on a large folded plate. With the aid of this graph it will be relatively easy to reduce from the older system of wave-lengths to the new one, and *vice versa*. However, since the data given by Rowland are inadequate, the next table contains a very complete set of wave-lengths of iron lines in the International System. These wave-lengths extend from 2212·7 Å. U. to 8863·75 Å. U., and the intensities, when known, are given both for the arc and for the spark. The next table, likewise of inestimable value, deals with the principal lines of all the elements, the interval having the limits 1854·04 Å. U. and $9{\cdot}0850^{\mu}$. The last table in the volume gives the wave-lengths of 2800 heads of emission band spectra together with symbols showing whether each band is shaded off towards the red or towards the violet. Furthermore, the presumable

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[*] See this Journal, vol. xxx, p. 349, 1910.

"origin" of each band is recorded. Such a table has never before appeared in the literature of the subject. The remarks prefatory to each of these special tables are very pertinent and illuminating.

Since this volume completes Kayser's magnificent contribution to the subject of spectroscopy, it may not be out of place to briefly reflect a portion of the last preface. When, in the year 1900, the author wrote the preface to the first volume he hoped to be able to incorporate all the important facts of physical spectroscopy in four volumes and to devote a fifth volume to astrophysics. The hypergeometric increase, so to speak, in the literature of the subject necessitated the expansion of the four projected volumes into six. Doubtless this great increase was largely due to the influence of Kayser's contributions. As regards the volume on astrophysical data and phenomena Kayser expresses himself as follows: "When I contemplate the astrophysical literature at my disposal it becomes at once apparent that the proposed single volume will not suffice even approximately; three volumes would be required, and I should need at least eight years in which to complete the work. I do not doubt for a single instant that I have grown too old to undertake such a task: the labor of my university office has increased, spare time has decreased, also my powers of endurance, and particularly my memory, are no longer as reliable as formerly, and without the latter a work of this kind cannot be written. Therefore, with deep regret, I have decided to bequeath to younger hands the presentation of the astrophysical applications, which interest me so very much, and I hope that a competent man will soon take up the task." Nevertheless, it is a source of great pleasure to read farther on that Kayser hopes to be able to revise the earlier volumes of his "Handbuch," and to continue his experimental investigations in the subject. H. S. U.

11. *Relations entre les Circulations Atmosphériques, l'Électricité Atmosphérique et le Magnétisme Terrestre;* by ALFRED VIALAY. Pp. x, 203, with 4 figures and 3 plates. Paris, 1911 (H. Dunod et E. Pinat).—The primary object of this monograph is to account for the existence of two points in the northern hemisphere and three in the southern which are characterized by being poles of low temperature, of maximum barometric pressure, of the great atmospheric circulations, of the aurorae, and of the earth's magnetic field. The first "book" is devoted to the question of the circulation of the atmosphere. The associated chapters deal with summer and winter in the northern and southern hemispheres and with the various types of wind-storms. As a practical application of the generalizations reached in the first book, the author accounts for the severe winter of 1879–1880, and for the mild, damp winter of 1909–1910, as experienced in France. In the second book the phenomena associated with atmospheric electricity are discussed at some length. Globular lightning, the aurorae, and other interesting manifestations are given due

attention. The chapters of the third book take up, in order, the distribution of magnetism at the earth's surface, the cause of terrestrial magnetism, the diurnal variations, and the secular changes. The author's style is pleasing and he presents the entire subject in a clear, logical manner. H. S. U.

12. *Magneto and Electric Ignition;* by W. HIBBERT. Pp. 154, with 79 figures. London and New York, 1912 (Whittaker & Co.).—This compact little volume gives effectively answers to all the most important questions which arise in connection with the details of construction and maintenance of such internal combustion engines as are used in automobiles, motor cycles, aeroplanes, etc. It is written in a popular style, and the small amount of electrical theory necessary is made as clear as possible by means of well-selected, familiar analogues. The book should be of great value to non-scientific readers who need practical, concise rules for locating faults in cells, electrical connections, spark-plugs, and other parts of the entire engine system. H. S. U.

13. *General Physics;* by W. WATSON. Pp. xiii, 564, with 311 figures. New York, 1912 (Longmans, Green and Co.).—This book has been written conformably to the author's opinion that a considerable number of the simpler physical phenomena, which are customarily included in a first course for general and technical college students, can be advantageously omitted, or dealt with very briefly, so as to save time and space for greater thoroughness in the treatment of the more important problems and of the recent developments of pure and applied physics. Attention is directed to the key-note of each paragraph by titles inset in heavy type at the margin of the text. The index is preceded by a generous list of questions and examples grouped to correspond to the "books" and chapters. The numerical answers are collected at the end of this list of exercises. The treatment is logical, the presentation lucid, and the diagrams are clear, but the type seems to be somewhat too small with the spacing compressed. We have noticed only one slip, namely, on page 357, "this phenomena." H. S. U.

14. *Gli Elettroni nei Metalli;* by LAVORO AMADUZZI. Pp. 147. Bologna, 1912 (Nicola Zanichelli).—This monograph, a companion to the author's previous publication, "Ionization and Electric Convection in Gases," covers the same field in the metals that the previous work did for gases. The conduction of electricity through metals, and other phenomena due to the presence of electrons in metals, are discussed from the theoretical standpoint. Some of the topics discussed are: conductivity; magnetism; relations of metals in contact with gases, liquids, and other metals; galvanic and thermo-magnetic phenomena; and the theory of electrons in relation to radiation. H. B. L.

II. GEOLOGY AND MINERALOGY.

1. *Thirty-third Annual Report of the Director of the United States Geological Survey*, GEORGE OTIS SMITH, Director. Pp. 17. —The advance sheets of this report have recently been issued (Dec. 18). They show that the appropriations for the work of the Survey for the fiscal year 1911–12 comprised items aggregating a little more than $1,500,000. The great need of the Department of a suitable Survey building, constructed to meet the needs of the Department, is taken up in detail. No one who has had direct knowledge of the very great difficulties under which the work of the Survey is now carried forward in its present quarters will fail to realize the importance of this matter. Lack of fresh air and light, restricted space, and other similar points affecting the general efficiency, are serious enough ; but first of all comes the risk from fire, about which warning has been given more than once in recent years. The fact that the value of the material now in the Survey building is inventoried at nearly $5,000,000 should lead Congress to take early action in the matter. Plans for a building such as the situation requires have been put before Congress and the estimates run from about $2,000,000 to nearly $5,000,000, according to proposed size and material of construction. It is greatly to be hoped that the matter may be speedily acted upon.

The Director remarks that while the work of the Survey has of necessity in recent years developed particularly along economic lines, strictly scientific work has not been neglected, in fact the two kinds of work must go forward hand in hand. He mentions a series of studies, in part published, in part nearing completion, which show the value of the work accomplished by the Survey for pure science. A number of these studies are on paleontology, conspicuous among them the monograph now being issued from the press on the Cambrian Brachiopods, by Dr. Walcott. Remarks are also made in regard to the progress of work on geologic folios, in land classification, and also of publications (often carried forward in coöperation with State Surveys) which have a definite educational value. The Director in closing states that : "Although the appropriations made directly for the Geological Survey showed an increase of only $30,480 over those of 1911, there was a notable increase in the amount of work done by the field service. The funds available through coöperation with other Federal bureaus and with the States amounted in 1912 to 27 per cent of the direct appropriations and showed an increase over coöperative funds of the preceding year of 42 per cent. This increase in the field work involved a large increase of the work in the Washington office, to which was added the greatly increased service rendered the Secretary's Office, the General Land Office, and the Office of Indian Affairs in connection with public-land administration."

2. *West Virginia Geological Survey;* I. C. White, State Geologist. *Doddridge and Harrison Counties;* by Ray V. Hennen, Assistant Geologist. Pp. xvi, 712; 25 plates, 5 figures, 3 maps in separate cover. Morgantown, 1912.—The excellent series of county reports issued by the Geological Survey of West Virginia has now been increased by a volume devoted to Doddridge and Harrison counties. These counties lie in the north-central portion of the State and embrace an area of nearly 740 square miles. In introducing the work of Mr. Hennen, the author of this volume, Professor White calls attention to the fact that in an earlier report Mr. Hennen's suggestions, based upon carefully made structural maps, have already led to the discovery of a large new oil pool; and he adds that similar discoveries of oil and gas pools are likely to follow from the work here detailed.

As implied in this statement, the chief permanent economic interests of the two counties lie in the oil wells, of which we have given the records, for example, of 240 wells in Doddridge County and 435 in Harrison County. In both cases the wells noted have been selected from a much larger number drilled, on account of their wide distribution and some special features associated with them. The coal production of this area is also an important matter, the amount mined in Harrison County in 1910 being 3,700,000 gross tons. This coal is confined to the Redstone and Pittsburgh beds, which though deeply buried in Doddridge and western Harrison, are brought within easy reach in the central and eastern portions of the latter county by the Wolf Summit and Chestnut Ridge anticlines. Another important industry in Harrison County is that of the glass companies which have grown rapidly in recent years, and taken together with the oil, gas, and coal production, and the farming interests, makes this the second richest county in the State.

This carefully written report by Mr. Hennen, aided by David B. Reger, goes not only into all the necessary details of the history and development of the industries mentioned, but gives further, in a series of chapters, a detailed account of the general geology. The stratified rocks exposed belong to the Dunkard, Monongahela and Conemaugh series of the upper Carboniferous. The concluding chapter is devoted to a study of the soils, made in coöperation with the United States Department of Agriculture.

In addition to numerous other illustrations, we have, in a separate cover, three large maps on a scale of 1/62,500. These are devoted respectively to the topography, agricultural soils, and the general and economic geology.

3. *Illinois State Geological Survey.* F. W. DeWolf, *Director. Bulletin No. 17. Portland-Cement Resources of Illinois;* by A. V. Bleininger, E. F. Lines, F. E. Layman. Pp. 121; 19 plates. Urbana, 1912.—The Portland cement industry has developed enormously in recent years, the production of the United States having increased from 8,480,000 bbls. in 1900 to 76,550,000 in 1910, the latter valued at $68,200,000. Illinois

produced about 4,500,000 bbls. in 1910 and the industry is still increasing; hence the interest of this bulletin, which describes the subject from its different standpoints. On the theoretical side, it is to be noted that the recent work of the Geophysical Laboratory in Washington comes in for discussion. Probably the most valuable part of the Bulletin is that dealing with the numerous localities arranged geologically from the Lower Magnesian limestone of the Ordovician to the LaSalle and Fairmount limestones of the Pennsylvanian.

The Illinois Survey has also issued the following: Bulletin 20. *The Carlyle Oil Field and Surrounding Territory;* by E. W. Shaw, U. S. Geol. Survey in coöperation with State Geological Survey. Pp. 37; plates II–VII. *The Carlinville Oil and Gas Field;* by Fred H. Kay, State Geol. Survey. Pp. 38–50; plates VIII–X. Urbana, 1912.

4. *Topographic and Geologic Survey of Pennsylvania;* R. R. Hice, State Geologist. *Report No. 5. The Talc and Serpentine of Northampton Co. and the Portland Cement Materials of the Lehigh District;* by Frederick B. Peck. Pp. 65; 17 plates, 9 figures.—The special area covered by this report embraces the central portions of Lehigh and Northampton counties in Eastern Pennsylvania, and extends across the Delaware river into Warren County, New Jersey. Two lines of work are followed out in detail; the first deals with the talc and serpentine deposits and describes their geological occurrence and also the uses to which they are put. The second takes up the cement industry, treating it both historically and from the practical side. It is interesting to note that the first Portland cement works of the United States were begun in 1879 at Coplay, Lehigh Co.; these, though small in the beginning, now manufacture from 2,000 to 3,000 barrels daily. Notwithstanding the rapid growth of this industry over the country at large, as noted above, the Lehigh district still yields about one-third of the total annual cement production of the United States.

5. *Report of Flood Commission of Pittsburgh, Pennsylvania, 1911,* containing the results of the Surveys, investigations and studies made by the Commission for the purpose of determining the causes of, damage by and methods of relief from floods in the Alleghany, Monongahela and Ohio rivers at Pittsburgh, Penn., together with the benefits to navigation, sanitation, water supply and water power to be obtained by river regulation. Pp. 452, illustrated with diagrams, plates, and maps in pocket.—The great Ohio valley flood of 1907 resulted in property losses amounting to more than $100,000,000 and spurred into aggressive action towns and cities that had theretofore looked on floods as a necessary, recurrent evil. The Inland Waterways Commission began to study the problem, and local commissions were appointed, the largest and most important being the Pittsburgh Commission. Its report is the most detailed, scientific, and the most valuable from the standpoint of legislative action, that has yet been pub-

lished in this country, on river control. It is practically an encyclopedia of flood data relating to the Pittsburgh region. The comprehensive way in which the problem has been attacked may be appreciated from the fact that even the secondary papers on forest conditions, rainfall, etc., in the Alleghany and Monongahela catchment basins, are the best that have yet been written for these districts. The studies of the topographic and soil conditions are well done, and at every step are correlated with the outstanding problems of the Commission. Furthermore each feature of the problem is handled in so broad a manner that the student looking for principles is as gratified as one looking for detailed information on a point of restricted interest. It would quite exceed the limits of space to review even the best portions of this great work. We shall confine ourselves to a brief statement of the principal results.

1. Floods at Pittsburgh are increasing in frequency and height.
2. The damage resulting from a flood of a given height is steadily increasing.
3. The direct losses due to flood damage at Pittsburgh amounted to over $12,000,000 in the last ten years, while in one year and five days, between March 15, 1907, and March 20, 1908, three floods occurred, causing a direct loss at Pittsburgh of about $6,500,000.
4. There are many favorable reservoir sites of large capacity available for flood-water storage on the drainage areas of Pittsburgh.
5. Forty-three sites have been selected and most of them completely surveyed by the Flood Commission, the others having been studied from existing topographic maps, and by means of partial surveys.
6. The estimates of the cost of storage reservoirs and other works for flood relief made by the Flood Commission are based on detailed surveys, and show that Pittsburgh can be completely safeguarded against floods at a cost of about $20,000,000.

In addition, it is proposed to build nearly 24,000 feet of protective wall along the lower margins of the river at Pittsburgh, to limit pier extensions that restrict the channel, and to take due account of forest influences on the run-off of both water and waste. I. B.

6. *The Trias of the Himálayas;* by C. Diener. Mem. Geol. Surv. India, xxxvi, part 3, 176 pages, 1912.—Professor Diener here presents a summary, with the necessary detail, of the Triassic of the Himálayan region. The lower (40–150 feet), middle (100–400 feet) and upper (1250–2750 feet) Triassic localities are taken up in succession and correlations are made with Europe, Siberia, North America and elsewhere. The work is of the greatest import to all students of Triassic faunas and their intercorrelations.

The geologists of India were agreed that the Triassic began with the Otoceras dark shales and thin limestone, until 1900, when Noetling stated that these beds and the entire Ceratite beds must be included in the Permian. Diener says that this latter view "soon turned out to be incorrect" (45). The Permo-Triassic boundary in the eastern Alps has also been under discussion, and Diener remarks :

"There is no unconformity between the Permian Bellerophonkalk and the shales of the lower Werfen (Seis) beds, but the lithological contrast between the two groups is rather sharply marked, considerably more so, as a rule, than between the Productus shales and the Otoceras stage (of India). Nevertheless sections have been found, where the Bellerophon limestone passes gradually into the overlying shales. * * * in the vicinity of Sarajevo a very interesting section has been described by E. Kittl, where a bed of limestone containing fossils of the Bellerophonkalk is intercalated in shales lithologically identical with those of the Werfen beds. It is evident that in this section the highest beds of Permian age are developed in the facies of the Triassic Werfen shales and that the lithological boundary does not coincide with the true limit of the two systems. * * *

"It is true that the genus *Otoceras* is known outside the Himálayas from Permian rocks only, a small number of species, represented by a few fragmentary examples, having been collected from a single locality (Julfa on the frontier of Persia and Russian Armenia). But there is not a single case of specific identity with Himálayan forms. The Armenian species of *Otoceras* are associated with a rich fauna of distinctly Palæozoic aspect. The numerous types of *Productidæ*, *Orthidæ*, *Spiriferidæ*, *Gastrioceras*, differ so widely from anything that is seen in the fauna of the Indian Otoceras beds, that the presence of the genus *Otoceras* at Julfa does not justify the assumption of its being restricted to the Permian" (48–9).

"Positive palæontological evidence is decidedly contradictory to the assumption of a Permian age for the Indian Otoceras beds. The general character of the cephalopod fauna is what we should expect to find in a Mesozoic horizon, the overwhelming majority of the ammonites being provided with ceratitic sutures. This character is not exhibited in any Permian cephalopod fauna hitherto known. * * *

"All the numerous types of Palæozoic brachiopods, which are the predominating and most characteristic element both in the Productus Limestone of the Salt Range and in the Kuling shales of the Himálayas, are completely absent from the Otoceras beds. There is no stratigraphical break in the uninterrupted sequence of beds which in the Himálayas connects the Permian and Triassic systems, but there is a distinct palæontological break or hiatus at the base of the Otoceras beds. In the Himálayan region there is certainly no gradual shading-off from a Palæozoic to a Mesozoic marine fauna through an intermediate group, but a sharply defined limit, which none of the characteristic species of Permian brachiopods transgresses. This absolute distinction between the brachiopods of the Kuling shales and of the Otoceras beds is so sharp that *the limit between the two faunæ offers itself as the most natural boundary of the two systems*" (50–51).

C. S.

7. *Origin and Antiquity of Man;* by G. FREDERICK WRIGHT. Pp. ix, 547; 42 illustrations. Oberlin, Ohio, 1912 (Bibliotheca Sacra Company).—In this volume the author discusses the limitations of the possible existence of life on earth, giving a probable duration of twenty-four million years and stating emphatically that it was not possible for life to have existed fifty million years ago. Post-Tertiary time, beyond which the evidence for man's existence is deemed inconclusive, is relatively short, so that "while the antiquity of man cannot be less than ten thousand, it need not be more than fifteen thousand years, as eight thousand years of prehistoric time is considered ample to account for all known facts relating to his development."

From the methods of scientific approach the author passes on to the historical evidence and the linguistic argument for man's antiquity. He then discusses the origin of the races of Europe and of the American Indian, followed by the significance of the glacial period in its relation to contemporaneous man. After weighing the evidence for the existence of Tertiary man, Mr. Wright, who is not a believer in the artificial character of eoliths, considers it unproven. Arguments of a physiological and psychological character are next discussed, together with the biblical documents, which, however, contain nothing in their chronology to prevent any extension of prehistoric chronology for which there is proper evidence.

In the summary and conclusions the author emphasizes the fact that despite the brevity of post-glacial time, history begins with a highly civilized condition of man, who now shows a tendency to degeneration which is counteracted only by acceptance of outside agencies. The origin of man by purely naturalistic means he considers inconceivable.

The general appearance of the book is not impressive. This is especially true of the paper upon which the volume is printed and of the half-tone engravings, some of which are very obscure.

R. S. L.

8. *Prehistoric Man;* by W. L. H. DUCKWORTH. Pp. viii, 156; 28 text figures and 2 tables. Cambridge, 1912 (University Press); New York (G. P. Putnam's Sons).—Doctor Duckworth, who is University Lecturer in Physical Anthropology at Cambridge, is abundantly able to speak with authority on the subject of prehistoric man, although in the work at hand he deals only with the earliest phases of human prehistory, ending his review with the close of the Aurignacian division of the Paleolithic age.

The chapters, of which there are but six, include: the precursors of Paleolithic man, in which *Pithecanthropus* and *Homo heidelbergensis* are described; Paleolithic man from the physical aspect; alluvial deposits and caves; associated animals and implements; human fossils; and finally, a summary of human evolution which, together with an excellent bibliography, closes the volume.

This little book, which is one of the Cambridge Manuals of Science and Literature, is well written and gives a very complete and concise summary of the present state of our rapidly growing knowledge of early human progress. R. S. L.

9. *Early Man in America;* by A. Hrdlička. Correction. The second paragraph from below on p. 553 of the above article should read as follows:

As to the part that theory played in this connection, it is sufficient to point to the system of human descent and migration constructed on the basis of the various finds, assumed to indicate the presence of early man in South America, by Ameghino. He derived the whole human family from certain little primitive forms in South America and peopled that continent with hitherto unsuspected species of man and genera of precursors. He asserted that Africa and Oceania were peopled by the descendants of a far distant South American precursor of man, the Triprothomo; and he assumed that a later spread of man from South America peopled America, Asia and Europe, resulting in the American, Mongolian and White races.

10. *Geology and Ore Deposits of the Park City District, Utah;* by John M. Boutwell. U. S. Geol. Survey, Prof. Paper, 77; pp. 229, 44 plates, 18 figures. Washington, 1912.—The Park City District is situated on the eastern slope of the Wasatch Range in the north-central part of Utah. The greatest geologic activity in the Wasatch Mountains took place at its junction with the east-west Unita Range. At this point extensive and irregular intrusion, wide extrusion, thorough contact metamorphism and much faulting have produced in a small area highly complex results. At the heart of this area have been formed the extensive and rich ore bodies of the Park City district.

The sedimentary rocks, which include sandstones, shales, quartzites, and limestones, range in age from the lower Carboniferous to Triassic. They have been cut, deformed and altered by a series of intrusive diorites and diorite porphyries in the form of laccolites, stocks, and dikes. Andesite flows are found on the outskirts of the district. At the south there is a great laccolithic intrusion of diorite with the sedimentary rocks lying on its flanks and dipping toward the north and east. These upturned sedimentary rocks are extensively faulted and intruded by stocks and dikes. The metamorphosed and hardened sedimentary rocks extend as a backbone in an east-west direction across the region and it is on their northern slope that the extensive ore bodies are found.

The ores, which are chiefly silver-bearing, consist of the usual lead, copper, and zinc minerals. The principal ore minerals are galena, tetrahedrite, sphalerite, and cerussite. The ores occur as lode deposits and as bedded masses in the sedimentary and intrusive rocks. They lie chiefly in the sedimentary rocks in close proximity to igneous intrusions and have been mostly deposited by means of replacement action. W. E. F.

11. *Oil-Finding; An Introduction to the Geological Study of Petroleum;* by E. H. Cunningham Craig; with an Introduction by Sir Boverton Redwood; pp. x, 195, 13 plates, 18 figures. New York, 1912 (Longmans, Green & Co.); London (Edward Arnold).—This small book has been written in order to emphasize the importance of the geological structure of oil fields and to assist the field geologist, the manager, and the investor in understanding the geological facts. It treats briefly of the origin of petroleum; its migration under ground after formation and the manner in which it is stored in the rock strata. It describes the characteristic geological structures of oil fields and the indications of the petroleum, both on the surface and in the bore holes. It explains the proper location of oil wells, and closes with two brief chapters of hints to the young field geologist who is to work in oil regions. It is a well-written and well-illustrated book and should prove a valuable one in its field. W. E. F.

12. *Examination of Prospects;* A Mining Geology; by C. Godfrey Gunther. Pp. vi, 222, 79 figures. New York, 1912 (McGraw-Hill Book Co.).—This hand-book is intended, as stated in the preface, "to present the practical side of economic geology concisely and in convenient form." The following chapter headings will serve to give an idea of the scope of the book: Mining Examination; Structural Geology; Structural Features of Ore Deposits; Primary Ores and their Distribution; Types of Primary Ore Deposits; Primary Ore Shoots; The Primary Alteration of Wall Rocks; Alteration by Surface Agencies; Residual Ores and their Distribution; Secondary Ores and Ore Shoots; Outcrops. The book properly places the emphasis upon known facts and touches only briefly theoretical considerations. It is amply and well illustrated and should prove a material help to the general mining engineer and prospector. W. E. F.

13. *Building Stones and Clay-Products. A Handbook for Architects;* by Heinrich Ries. Pp. xv, 415; 59 plates, 20 figures. First edition. New York, 1912 (John Wiley & Sons); London (Chapman & Hall, Ltd.).—The present author is well known for his numerous and important contributions particularly to matters concerning the clay industries of the country. In this volume he covers a field somewhat broader in extent, presenting facts that are necessary for the knowledge of the architect with reference to the prominent building stones, as well as bricks, terra cotta, tiles, etc. While the object and scope of the volume do not permit exhaustive treatment, a wide range of important facts is presented in a clear and simple form, so that the whole work is an excellent summary of the subject which it covers. It is profusely illustrated and fills admirably the field for which it is designed.

14. *Mineralogy, an Introduction to the Theoretical and Practical Study of Minerals;* by ALEXANDER H. PHILLIPS. Pp. viii, 699, with 534 figures. New York, 1912 (The Macmillan Company).—Another extensive work has been added to the literature on Mineralogy, one that is planned to give the student all that he needs to prepare him to go on and use advanced methods and the advanced literature. Part I (pp. 1–218) deals with Crystallography in the broad sense, including not only a description of the various types of crystals but also their optical properties. The generally accepted definitions as to symmetry are applied to the thirty-two different types, but the idea of hemihedrons, which has certain advantages as presenting the subject simply to the student, is also employed ; mathematical solutions of problems are not introduced. The figures are clear and well drawn, but the printer has occasionally taken the liberty to throw them out of the vertical position (e. g. fig. 34), a painful experience that other authors have often had.

Part II (pp. 219–545) is given to Descriptive Mineralogy ; this begins with brief chapters on the relations of minerals to the elements, their origin and physical properties, and then some 225 selected species are described in detail. Half-tone figures, some of them admirable but others less so, accompany the descriptions; the schematic figures usually used to show the varying habit of crystals are not introduced.

The subject of Determinative Mineralogy occupies Part III and is discussed in detail. The general blow-pipe table here given includes all but a very few rare species, so that the student has the advantage of having presented to him practically all known species with brief characterization of each. A table for the determination of common minerals by their physical properties is also given embracing about one hundred and fifty species.

III. ZOOLOGY.

1. *Comparative Anatomy of Vertebrates;* by J. S. KINGSLEY. Pp. ix, 401, with 346 illustrations. Philadelphia 1912 (P. Blakiston's Son & Company).—Teachers of comparative anatomy have long felt the need of a suitable text-book on the subject by an American author. This new book by Professor Kingsley exactly meets the requirements by presenting in concise form and with adequate illustrations the essential features of the morphology of the organ systems of the vertebrates. The embryological history is the basis on which the subject matter is arranged, and the comparisons are then followed through the classes of vertebrates. The use of smaller type for the less general portions of the subject and the printing of technical words in heavy-faced type add greatly to the usefulness of the book from a pedagogical standpoint.

The illustrations, which are of so much importance in a work of this kind, are of great merit. Many of them are new, and most of the others have been redrawn from original sources. The stereograms and drawings of models are especially helpful. An excellent feature in this connection is the selection of illustrations from species not usually dissected in laboratory courses. The student is thus relieved of any temptation to copy the figure instead of making his drawing from his own dissection.

For the investigator the book contains an extensive bibliography, and for the student a list of definitions of systematic names. W. R. C.

2. *An Introduction to the Study of the Protozoa, with special reference to the parasitic forms;* by E. A. Minchin. Pp. xi, 517, with 194 illustrations. New York (Longmans, Green and Co.); London (Edward Arnold), 1912.—The author, one of the foremost authorities on protozoology, here presents a general summary of the present state of our knowledge of the unicellular animals. The comparatively recent discovery that the Protozoa are the cause of so many of the most fatal diseases of man and animals makes a knowledge of this group of greater importance to the human welfare than that of almost any other group of animals.

The introductory chapters contain an excellent account of the characters and modes of life of different families. The succeeding chapters describe the details of the organization of the body of the protozoa in general. Then follows a discussion of the reproductive processes, syngamy and sex, polymorphism and life cycles, and general physiology. The last half of the book contains a systematic account of the various classes, including the structure, habits, and life cycles of a large number of typical species. As the parasitic forms have been most fully studied they are described in greatest detail, with emphasis on their remarkably complicated modes of reproduction, and their means of distribution to the host in which they cause disease, A classified bibliography of over 900 titles concludes the work.

The subject is presented in such a manner as to be easily understood by the general reader who has some knowledge of biology, and the book should prove of particular value to the medical man in showing him the nature of the organisms which he endeavors to subdue in the treatment of the diseases which they cause. The professional biologist and zoologist will also find here a vast amount of information hitherto obtainable only by reference to numerous technical reports. W. R. C.

3. *Compound Ascidians of the Coasts of New England and Neighboring British Provinces;* by Willard G. Van Name. Proc. Boston Soc. Nat. Hist., vol. xxxiv, pp. 339–424, with 6 plates.

Simple Ascidians of the Coasts of New England and Neighboring British Provinces; by Willard G. Van Name. Proc. Boston Soc. Nat. Hist., ibid., pp. 439–619, with 31 plates.—These two monographs contain an account of all the Ascidians known from the northeast coast of America. The work is based on the collections belonging to the United States National Museum and the Peabody Museum of Yale University. Most of the specimens were collected by Verrill, Smith, Webster and Harger in 1868–70, and by the United States Fish Commission during the years 1871–87. The number of species in both groups is only 49, of which 15 are compound Ascidians, belonging to 13 genera. Of the 34 species of simple Ascidians representing 12 genera, 5 species are new to science. Three additional species, of which 2 are new, collected in the deep-sea area, are included. Each of these is carefully described with reference to the external and internal anatomy, and fully illustrated by photographs and drawings. The nomenclature is revised, and the previous confusion of names eliminated.

Similar studies on the other groups of our marine invertebrates are greatly needed. W. R. C.

4. *The Early Naturalists: Their Lives and Work* (1530–1789); by L. C. Miall. Pp. xi, 396. London, 1912 (Macmillan and Co.).—To one who is familiar with the historical development of the biological sciences, the names of the earlier naturalists suggest little more than the discoveries for which they are renowned. That they lived as did other people of their time, and made their discoveries only by laborious struggles against the ignorance and prejudice of the masses, and with the crudest of tools, is rarely considered. The author of this interesting book may be said to have made the acquaintance of these older naturalists by spending his leisure hours for some years among their voluminous writings. And with this volume he introduces the reader to the man—not merely to the investigations which the man made, but to his daily life. It is with real pleasure that one shares Malpighi's elation over wonders which his newly-invented magnifying glasses daily revealed, and one grieves with John Ray in his persecutions by the church, and in the blighting of his promising career at Cambridge. The reader can see Leeuwenhoek, in 1683, discovering the first known bacteria, which he obtained from his own teeth, and one is reminded of modern times when the swindler tries to sell him a microscope in the lens of which small living worms were so skillfully fastened as to deceive the observer.

The subject is arranged chronologically, embracing the lives of the founders of modern biological science: Brunfels, Ray, Hooke, Malpighi, Swammerdam, Redi, Reaumur, Linnaeus, Buffon, and many less distinguished naturalists of the 16th and 17th centuries. During this period occurred the revival of learning, the invention of the microscope, the study of comparative anatomy, the classification of organisms, and the popularization of natural history. The observations and experiments, whether success or failure, accomplished by each of the naturalists of these times are described, and their importance in the future development of the science is indicated. W. R. C.

5. *Teachers' Manual of Biology;* by MAURICE A. BIGELOW. Pp. ix, 113. New York, 1912 (The Macmillan Company).—This is a helpful little book of suggestions to teachers of biology. The methods of obtaining and preparing materials for a course of laboratory exercises are described, together with many valuable hints on the presentation of the different phases of the subject in the classroom. The book is particularly designed to accompany Bigelow's recent text-book, "Applied Biology," the chapters and paragraphs being numbered correspondingly. Lists of books, apparatus, and dealers in supplies are given in appendices. W. R. C.

6. *Michigan Bird Life;* by WALTER BRADFORD BARROWS. Pp. xi, 822. (Special Bulletin of the Department of Zoology and Physiology of the Michigan Agricultural College.) Published by the Michigan Agricultural College, 1912.—This book contains a systematic account of the 326 species of birds found in the State of Michigan. In addition to the technical description of each species, a large amount of attention is devoted to the habits, food and economic importance. The work is illustrated with 70 plates and 152 text figures of anatomical details. The natural history of each species is written in an entertaining style, and the book is thus in wide contrast to the ordinary catalogues of birds which so many state surveys have published.

W. R. C.

IV. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *The Physiology of Protein Metabolism;* by E. P. CATHCART. Pp. 1–142. New York, 1912 (Longmans, Green & Co.).—This publication is of the series of Monographs edited by Plimmer and Hopkins and the attempt has been made in the present volume to avoid laying undue stress upon the fate of particular constituents of the protein molecule. Instead it consists of a discussion of the more important results in the problems of protein metabolism that have been published within the last decade. Some of the topics discussed are digestion and absorption of proteins, protein regeneration, deamination, influence of food on the composition of the tissues, protein requirements, theories of protein metabolism, starvation, work. F. P. U.

2. *Researches on Cellulose, III, 1905–1910;* by CROSS and BEVAN. Pp. x, 173. New York, 1912 (Longmans, Green & Co.).—This is the third in the series of volumes supplementary to the authors' "Cellulose." In this last volume no attempt is made to present a complete review of the extensive literature dealing with the various celluloses and their technical uses; the authors have confined themselves to a critical review of a relatively few pieces of work in the field of cellulose chemistry which they believe contribute most directly to the solution of fundamental problems. There is an introduction, distinctly metaphysical in

character, followed by chapters on Normal Cellulose, Cellulose Esters, Ligno-Celluloses and Technical Developments. A. L. D.

3. *The Chemical Constitution of the Proteins*; by R. H. A. PLIMMER, D.Sc. Part I., Analysis. Second edition. Pp. xii, 188. New York, 1912 (Longmans, Green and Co.).—The new edition of this valuable reference book will keep the reader in touch with the continuous work on the chemistry of proteins carried on during the past few years. Although in no sense a volume to be read as a story, the monograph is far more enjoyable as a literary product than the usual collection of statistical data and analytical procedures. Facts are interspersed with viewpoints; and the historical aspects of the development of protein chemistry are not overlooked. Dr. Plimmer has exhibited a broad knowledge and not a little critique, so that his contribution can justly be classed among those few books which we dignify with the expression "authentic." The bibliography is unique and comprehensive. L. B. M.

4 *Microbes and Toxins*; by Dr. ETIENNE BURNET of the Pasteur Institute, Paris. Translated from the French by Dr. CHARLES BROQUET and W. M. SCOTT, M.D. Pp. xvi, 316, illustrated. New York and London, 1912 (G. P. Putnam's Sons).—A volume dedicated to Dr. Roux and provided with an introduction by Dr. Elie Metchnikoff can scarcely fail to attract the attention of the ever-growing number of readers to whom the wonders and mysteries of the new bacteriology provide an unfailing source of interest. In addition to the up-to-date discussion on the general functions of the micro-organisms—their form and behavior in the most varied environment—much space is given in this book to a presentation of the varied relations of these lower forms to man. Infection and immunity, toxins, vaccines, immune sera, chemotherapy, all find a place in this popular review. One will look in vain in some of the chapters for mention of classic researches from American laboratories; but American scientists have become accustomed to such omissions in foreign publications. A glossary forms an unusual, but useful, appendix to this popular exposition of some of the contributions of a rapidly developing science. L. B. M.

5. *Nutritional Physiology*; by PERCY G. STILES. 12mo, pp. 271, illustrated. Philadelphia and London, 1912 (W. B. Saunders Company).—It is refreshing to find a text-book of physiology which departs from the conventional lines and presents the story of animal functions from an original viewpoint. The sequence of the chapters in this volume is made to hinge upon the significance of the energy transformations in the body. Anatomical considerations properly form a very subordinate part in the discussions of the mechanical movements and chemical changes which characterize nutrition in its broadest sense. The chapter on alcohol is both rational and appropriate—in decided contrast with much of the unscientific nonsense commonly taught under stress of legal requirements. Professor Stiles' volume, with its numer-

ous touches of historical reminiscence and personal experience, can be highly recommended to teachers as an antidote to the familiar uninteresting elementary treatise and a guide to wider reading. It is dedicated to Graham Lusk. L. B. M.

6. *Oxidations and Reductions in the Animal Body;* by H. D. Dakin. Pp. viii, 135. New York, 1912 (Longmans, Green and Co.).—This volume represents a venture into a comparatively new field. Physiologists, on the one hand, have been too prone to think of chemical changes in the body in terms of supposed simple reactions that can be hastily labelled with some vague expression like hydrolysis, oxidation, deamination, or reduction. The chemist, on the other side, has often failed to grasp the limitations of reaction set by a biological environment. In Dr. Dakin's monograph we have an attempt at interpretation of biochemical processes by one who appreciates the importance, the difficulties, and the limitations of the subject. As one of the pioneer compilations the book furnishes not only a wealth of significant details, but also a series of carefully weighed deductions and highly suggestive viewpoints. It is novel in its aims and excellent in content. An elaborate bibliography is appended. L. B. M.

7. *Soil Conditions and Plant Growth;* by Edward J. Russell. Pp. viii, 168. New York, 1912 (Longmans, Green and Co.).—The relation of the soil to plant growth is involved with so many factors which represent variables in a problem of extreme complexity that it is difficult to find any treatise which deals with the broad subject in a comprehensive and, at the same time, critical spirit. Too often the topics have been approached with the prejudice that tends to adhere to anyone who has devoted his attention primarily to one aspect of any subject. He sees with the eyes of the chemist or botanist or geologist or microbiologist alone, and fails to realize that in the questions of soil function an ensemble of diverse fields in science is involved. The result of a narrow attitude is reflected in much of the controversy on the subject of soils that now pervades the literature. Dr. Russell's book, leaning in a chemical direction, shows a good perspective, a sane judgment, and a broad experience. The chapter on the historical development of the study of the growth of plants is an interesting review. The monograph furnishes a readable account of the present status of the subject to the layman; while the expert will find guidance and suggestion in the viewpoints and the extensive references to published contributions. L. B. M.

8. *The Protein Element in Nutrition;* by Major D. McCay, Professor of Physiology, Medical College, Calcutta. New York, 1912 (Longmans, Green & Co.); London (Edward Arnold). Pp. xv, 216.—This volume is essentially a review and critique of Chittenden's views regarding the quantitative role of protein in the dietary. The author has collected numerous valuable data regarding the food and metabolism of various races in India, particularly those living on a low plane of nutrition and thus

exemplifying on a large scale the lower protein intake which has been advocated by Chittenden as the outcome of his experimental researches. On the ground of his newer evidence of the inferiority of the Indian races or tribes existing on the lower dietaries McCay believes that the views of Chittenden are untenable; and he takes occasion to criticize some of the deductions which Chittenden has drawn from his own researches, as well as to point out features in the American investigations which seem to speak against the newer contentions. The problem is one that calls for careful physiological analysis and must be emancipated from the domination of mere opinion or prejudices in matters of nutrition. Hitherto there has been too much of the sentimental and too little of the scientific in the advocacy of schemes of diet. The present book is one of the newer contributions which speaks for a more rational attitude towards the problems at issue. The final word is, however, not yet spoken. L. B. M.

9. *Principles of Hygiene;* by D. H. BERGEY, M.D. Fourth edition thoroughly revised. Pp. 529, illustrated. Philadelphia and London, 1912 (W. B. Saunders Company).—Few individuals can be expected to-day to master the many diverse fields of science which are encompassed in the modern discipline of hygiene. This may serve to explain why there so few satisfactory text-books on the subject and to excuse the obvious inequalities of the various chapters of the volume by Bergey. To present the subjects of heating and sewage-disposal; soils and diet; immunity and water-supplies; clothing and naval hygiene; habitations and exercise, in the limits of a book of ordinary size and in an effective, authoritative and up-to-date fashion is no mean accomplishment. This volume excels in those subdivisions which relate more directly to the author's personal experience. It affords a convenient survey over the entire field; while for some of the divisions the critical reader will doubtless find it of advantage to consult special monographs. The range of topics is a very broad one; but some of the chapters could be greatly improved by a more radical revision. This is conspicuously true, for example, of the section on food and diet where one reads of mineral waters as "regulators of energy" and that fats serve "as nutrition to the nervous system." L. B. M.

10. *An Essay on Hasheesh;* by VICTOR ROBINSON. Medical Review of Reviews. Pp. 83. New York, 1912.—A semi-serious historical account of the distribution of *Cannabis indica*, its use in medicine and its employment in the production of hasheesh debauches. The account is interspersed with enlivening bits of wit, and includes a graphic description of the exhilarating effects of this subtle drug observed after its administration to men—among them the author. It is doubtful whether the publication of such questionable experiments in drugdom serves any commendable purpose. L. B. M.

11. *Geological Society of America.*—The twenty-fifth annual meeting of the Geological Society is held at New Haven, Conn.,

on December 28–31. Professor H. L. Fairchild, the president, delivers the presidential address on "The Pleistocene Geology of New York."

The Paleontological Society holds its annual meeting in connection with that of the Geological Society.

12. *American Association for the Advancement of Science.*—The sixty-fourth meeting of the American Association is held in convocation-week, from December 30, 1912, to January 4, 1913, in Cleveland, Ohio. Dr. Edward C. Pickering, Director of the Harvard College Observatory, is the president. Numerous affiliated societies meet at the same time.

OBITUARY.

SIR GEORGE HOWARD DARWIN, second son of the late Charles Darwin, died on December 7 in his sixty-eighth year. He was Plumian professor of astronomy at the University of Cambridge since 1883 and his original work in the departments of astronomy and mathematics was of the highest character.

EBEN J. LOOMIS, for fifty years (1850–1900) assistant in the Nautical Almanac Office of the Navy Department, Washington, died on the 2d of December at Observatory House, the residence of his son-in-law, Prof. David Todd, at Amherst, Massachusetts. Besides being a mathematician and astronomer, Mr. Loomis was a keen observer of nature, having been an early pupil of both Louis Agassiz and Asa Gray. His remarkable discovery of a flexing movement of the frond of *Asplenium trichomanes* brought him a most interesting letter from Charles Darwin. His *Eclipse Party in Africa* (1896) was reviewed in this Journal (vol. iii, p. 80). Among his other works were *A Sunset Idyl and Other Poems* (1903), and *Wayside Sketches* (1894).

EDWIN SMITH, the astronomer, died on December 1 in his sixty-first year. He was a member of the staff of the Coast and Geodetic Survey from 1870 to 1895 and was active in astronomical work, carrying on extensive observations on the force of gravity, on latitude determinations and related subjects.

Dr. WILLIAM A. BUCKHOUT, Professor of Botany in the Pennsylvania State College, died on December 3 at the age of sixty-six years.

Dr. JOHN MONROE VAN VLECK, Professor of Mathematics at Wesleyan University from 1853 to 1904, died on November 4 at the age of seventy-nine years.

Dr. RAMSAY H. TRAQUAIR, the zoologist and paleontologist, died at Edinburgh on November 22 at the age of seventy-two years.

WILLIAM FORSELL KIRBY, the English entomologist, died on November 20 in the sixty-ninth year of his age.

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VOL. XXXV. FEBRUARY, 1913.

Established by **BENJAMIN SILLIMAN** in 1818.

THE
AMERICAN
JOURNAL OF SCIENCE.

FOURTH SERIES

VOL. XXXV—[WHOLE NUMBER, CLXXXV].

No. 206—FEBRUARY, 1913.

NEW HAVEN, CONNECTICUT.

1913.

THE TUTTLE, MOREHOUSE & TAYLOR CO., PRINTERS, 123 TEMPLE STREET.

Published monthly. Six dollars per year, in advance. $6.40 to countries in the Postal Union; $6.25 to Canada. Remittances should be made either by money orders, registered letters, or bank checks (preferably on New York banks).

THE

AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

Art. XII.—*The Effect of a Magnetic Field on Ionization Currents;* by William Duane.

The effects produced by a magnetic field on the passage of electricity through gases in the arc and spark discharges and in vacuum tubes have been studied in a great many ways, and many important conclusions have been drawn from the experiments. In particular it has been found possible to determine the ratios of the charge e to the mass m of the particles that carry the positive and negative electricity in vacuum tubes. Further, Marx[*] has observed a transverse electromotive force (analagous to the Hall effect in metals) due to the action of a magnetic field on an electric current flowing through a flame.

About two years ago the writer undertook to investigate the effect (if any exists) produced by a magnetic field on ionization currents, in which the ionization is due to X-rays and radium rays. It was hoped that accurate measurements could be made from which the ratios e/m for the positive and negative ions could be calculated, and that evidence could be gathered either for or against the supposition that positive electrons exist, which are common to all gases. Some results of preliminary experiments were communicated to the French Academy of Sciences[†] in July, 1911, and the object of this paper is to give a description of these experiments.

The general principles underlying the methods of investigation may be stated as follows: A narrow and intense beam of α- and β-rays from radium emanation passes parallel to and midway between two parallel metal plates. An electric battery

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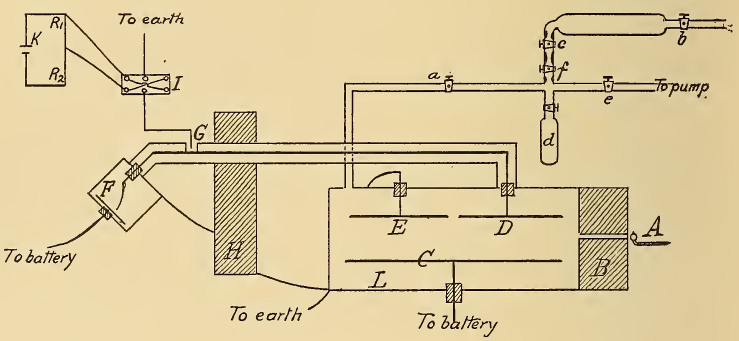
[*] Ann. der Phys., ii, 798, 1900.

[†] Comptes rendus, clii, 336–339, July, 1911.

maintains one of the plates at a constant potential, and a sensitive electroscope connected with the other serves to measure the ionization current between them. An air-tight box surrounds the plate, and by reducing the gas pressure in it the length of the mean free path of the ions can be increased. The box is suspended between the poles of an electromagnet in such a way that the lines of magnetic force are parallel to the metal plates and perpendicular to the beam of rays. Under these conditions an ion, after it has been formed, moves under the action of electric and magnetic forces that are at right angles to each other, and instead of following the line of electric force it is deflected off to one side by the magnetic field. If the length of the free path is long enough, and the magnetic force large enough, the ion should be deflected so far to one side that it does not reach the plate serving as electrode. Thus under proper conditions the magnetic field should diminish the ionization current measured by the electroscope.

Fig. 1.



The magnetic field, of course, deflects the β-rays and the secondary rays, and thus diminishes the current; but the ionization due to these rays is small compared with that due to the α-rays (which are not suppressed by the magnetic force), and it will be seen from the experiments that the decrease in the current due to the stopping of the β- and secondary rays is small and easily distinguished from that due to the deflection of the ions.

Figure 1 represents the arrangement of the apparatus. A tiny glass bulb A containing radium emanation (sometimes as much as that in equilibrium with 0·2 gram of radium) serves as the source of the ionizing rays. The glass bulb is supported close to a small mica window, 1^{mm} in diameter, and both the glass and the mica are so thin (their combined power of absorption not exceeding that of 3^{cm} of air at atmospheric pressure) that the a-rays from the emanation pass through them both. After passing through the window the rays enter the ionization chamber through a narrow slit in the lead block B. The vertical dimension of this slit is everywhere 1^{mm}, and its horizontal dimension (i. e., normal to the plane of the diagram) increases from 1^{mm} at the outer to 10^{mm} at the inner surface of the block. The lead stops all but the very penetrating γ-rays; and thus the ionizing rays are confined practically to a narrow beam midway between the plates C, D, and E. A battery of small accumulators keeps the plate C charged to any desired potential, plate D serves as the electrode, and plate E, which is put to earth, acts as a sort of guard to the electrode against the effects of secondary rays produced by the a-rays striking the end of the box. The a-rays do not touch the plates, and therefore the possible effects of secondary rays at the surfaces are eliminated. In order to protect the wires connecting the electrode D with the Wilson electroscope F from ionization currents due to the penetrating γ-rays, they are completely embedded in pure paraffine except for a small space G where a contact make and break allows the electrode to be put to earth or charged to any desired potential. To shield the electroscope itself from the γ-rays, a lead block H about 4^{cm} thick is interposed between it and the source of rays, and further the electroscope is not placed in the direct line of the beam of rays passing through the slit, but a little to one side, and in such a position that to reach the electroscope the γ-rays from the source have to pass through not only the two lead screens B and H but also one of the pole pieces of the electromagnet used to produce the magnetic field. These precautions taken, the direct influence of penetrating γ-rays is scarcely perceptible and quite negligible. To protect against electrostatic influence the paraffine covering the lead wires is incased in metal tubes and these together with the metal box L containing the plates and that containing the electroscope are put to earth. The entire ionization chamber with its plates and mica window, etc. lies between the poles of an electromagnet in such a position that the lines of magnetic force are normal to the plane of the figure. The two plates D and E are each 5^{cm} long and 3^{cm} broad, and the distance between them and C is 2^{cm}.

I have found the following method of using a Wilson electroscope accurate and reliable. The gold leaf is connected through the contact make and break G, not directly to earth, but to a reversing key I, which in turn is connected as shown to earth and to two points on an electric circuit K containing the resistances R_1 and R_2. After choosing suitable values for R_1 and R_2, one can change quickly the potential of the gold leaf from any desired positive to an equal negative value (or vice versa) simply by reversing the key I. In making measurements one notes the positions of the image of the gold leaf on the scale of the reading telescope, corresponding to small equal positive and negative potentials; then, breaking the contact at G, one measures the time required for the image to pass from one of these positions to the other. The total change in the potential of the gold leaf divided by the time is, of course, practically proportional to and a measure of the current. On closing the key G and verifying the positions of the image on the scale one can immediately detect, and correct for, any change in the zero or the sensitiveness of the instrument.

In order to be sure that the current observed is due to the ionization of the gas under investigation and not to foreign gases or secondary rays or other disturbing causes, I adopted the method of filling the ionization chamber represented in the figure. In the first place the gases in the ionization chamber should be pumped out and kept pumped out long enough to remove the greater part of the gases occluded in the metal surfaces. On beginning an experiment the stopcock "a" is closed and the system of tubes including the mercury pump is filled through drying tubes containing H_2SO_4 and P_2O_5 with the gas to be investigated. With the stopcock "b" closed this gas is then pumped out, and the process repeated several times. When, during the final pumping, the pressure has decreased to several millimeters of mercury, the stopcock "c" is closed, thus leaving a small quantity of gas in the reservoir "b c," and after this the best vacuum obtainable with the mercury pump is produced in the rest of the apparatus including the ionization chamber and the reservoir "d," which contains carbon, the gases in the carbon having been removed by previous prolonged heating to a high temperature in a vacuum. Finally, the mercury pump being cut off by the stopcock "e," the pressure is reduced still further by cooling the reservoir "d" with liquid air. If one measures the ionization current during the time the carbon is absorbing the residual gas, one finds that this current gradually decreases, sometimes changing sign, and after about an hour reaches a value that can be detected, but is negligible compared with the currents to be measured. When this condition has been reached, the reservoir "d" is cut off by closing its stopcock, and the stopcocks first "c" and then "f" are opened and closed several times, admitting each time to the ionization chamber the small quantity of gas between them. This process is repeated until the ionization currents become sufficiently large to be measured, and the required pressure obtained. By this method one can be sure that the currents are really due to the ionization of the small quantities of gas let into the ionization chamber. The pressure obtained after a given number of manipulations of the stopcocks "e" and "f" is estimated by means of a special series of experiments in which the pressure has been measured by the MacLeod gauge attached to the mercury pump.

The method of blowing the little glass spheres containing the emanation was perfected in collaboration with Mr. S. C. Lind.* It may be more or less similar to the method previously used by Rutherford and Royds† in making the thin-walled tubes used in their experiments on the α-rays. We have not seen, however, a description of their method. A glass tube is drawn out in or near a flame until it has a diameter of from $0{\cdot}2-1^{mm}$ and a wall thickness of from $0{\cdot}02-0{\cdot}1^{mm}$. The size and wall thickness of this tube determine the size of the sphere that can be blown from it. The end of the tube being sealed in the flame, it is inserted inside a larger Jena-glass tube ($1-2^{cm}$ in diameter), which is clamped in a horizontal position and heated on the outside by the hot flame of a large Bunsen burner. By means of a foot-blower a considerable pressure is maintained inside the capillary tube, and when the tip of this tube arrives at the part of the Jena-glass tube heated by the flame a little sphere begins to grow slowly. If the walls of the capillary tube are not thin enough to begin with, they may be drawn out thinner in the Jena-glass oven, the foot-blower being used to create a small pressure inside the capillary tube. By this method tubes may be drawn so thin that they show brilliant interference colors, and yet stand the pressure of the atmosphere with a vacuum inside. The sphere also can be made as thin as this, but they do not stand the pressure of the atmosphere as well as the tubes.

The glass at the end of the capillary tube, when it was sealed, leaves a thick spot on the surface of the sphere, and for this reason it is better to use the α-rays passing out at the side as represented at A in fig. 1. To bend the capillary tube at the proper angle a tiny gas jet about 1^{mm} long at the end of a fine glass tube may be used.

The condensation of the emanation into the small glass sphere presents some difficulties, for it is desirable, on account of the decay of the emanation with the time, to remove the gases, oxygen, hydrogen, carbonic acid gas, etc., given off by the solution of radium salt and the vessel containing it, as quickly as possible. I tried a number of methods of purifying the emanations and finally adopted a slight simplification of the method employed by M. Debierne. M. Debierne‡ per-

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* Sitzungsber. Akad. Wiss. Wien, cxx, IIa, December, 1911.

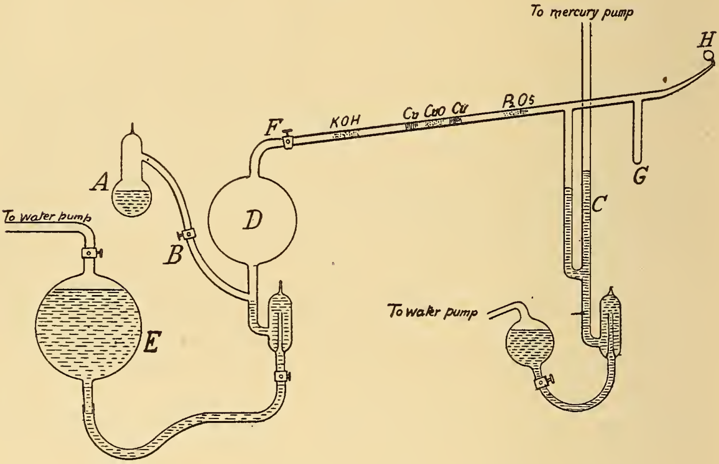
† Phil. Mag., xvii, 281, 1909.

‡ Ramsay and Soddy, Nature, July 16, p. 246, 1903; Proc. Roy. Soc., lxxii, 204, 1903; lxxiii, 346, 1904. Debierne, Comptes rendus, 14 Aug. 1905.

fected methods used by Ramsay and Soddy in their early experiments on helium, and the purification of the emanation in which the oxygen and hydrogen were absorbed by red hot copper and copper oxide, the carbon dioxide by caustic soda and the water vapor by phosphorus pentoxide, and the traces of gas remaining were removed by a vacuum pump after condensing the emanations by means of liquid air.

The apparatus is represented in fig. 2. The bulb A contains a solution of over ·3 gram of RaCl$_2$, kindly placed at my disposal by Madame Curie, and the emanation is allowed to accumulate in it with the stopcock B closed. When about to begin the purification, the mercury in the tubes C is lowered, and a good vacuum produced by means of the mercury pump. Toward the end of the pumping the tubes to the right of the caustic potash, including the copper and copper oxide, are thoroughly heated in order to expel all gases as far as possible. After a high vacuum has been obtained the mercury pump is cut off by letting the mercury rise in the tubes C, and the stopcock B is opened, allowing the gases from the solution, carrying with them the emanation, to enter the large reservoirs D and the purifying tubes. To absorb the oxygen and hydrogen the part of the tube containing the copper and copper oxide must be heated to a very dull red, and during the process, the stopcock B being closed, the mercury from C is allowed to rise into D, filling it and the tube up to the caustic potash. The stopcock F may be used to regulate the flow of gas into the purifying tubes. If desired, the small quantity of

Fig. 2.



gas left in the reservoir A may be extracted by lowering the mercury in D and repeating the process. It will be noticed that after the mercury has pushed the gases beyond F, the emanation does not come in contact with the grease of any stopcock. This is important, for the emanation decomposes the grease-producing gases. The heating of the copper and copper oxide should be continued until the pressure indicated by the columns of mercury in the tubes C ceases to diminish, after which the copper and copper oxide are allowed to cool, and the tube G is surrounded by liquid air. When the emanation has been sufficiently condensed in G, the communication with the mercury pump through the tubes C should be opened several times, for a few seconds only each time, until a high vacuum has been obtained. If this communication is left open a long time, part of the emanation evaporates into the pump and is lost. Finally, on removing the liquid air the mercury may be allowed to flow into the tubes through F and afterwards through C, pushing the emanation up into the little bulb H. The tube G should be large enough for the mercury to drop into without imprisoning emanation.

Using this method, it is not difficult to condense the quantity of emanation in equilibrium with 0·2 gram of radium chloride into a volume of 0·2 – 0·3 cubic millimeters. This volume is considerably larger than that of the emanation itself, and therefore the latter is not chemically pure. The process of condensation, however, need not last longer than about two hours, which is advantageous for certain purposes. To obtain the emanation chemically pure, the gases should be left in contact with the chemicals for a long time, and some such process of fractional distillation as those employed by Rutherford* and Debierne† should be used.

The effects produced by the magnetic field on the ionization currents may be stated briefly as follows: In the first place there is an enormous difference between the positive and negative currents. The magnetic force diminishes the value of the negative current very appreciably even at pressures of several centimeters; and at low pressures (less than $0{\cdot}06^{\mathrm{mm}}$) a field of a few hundred gauss reduces it to a small fraction of one per cent of its value. This is true of hydrogen as well as air. On the other hand, I have not observed any effect of the magnetic field on the positive current in air with pressures above $0{\cdot}03^{\mathrm{mm}}$, except that there is always an initial drop of about 5 per cent for small magnetic fields, due undoubtedly to the suppression of β- and perhaps secondary rays.

If the pressure is of the order of several thousandths of a

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* Phil. Mag. 1908.

† See Madame Curie, Traité de Radioactivité, I, pp. 312–321.

millimeter, and the electric force is not much greater than 10 volts per centimeter, magnetic fields of over 1000 gauss diminish the positive current in air very perceptibly. With an electric force of 25 volts per centimeter, however, no effect is produced by the magnetic field up to 2600 gauss, apart from the initial drop.

In hydrogen the effect is much more pronounced than in air, and takes place also under larger electric forces.

The fact that in air no effect except the initial drop is produced by the magnetic field, if the electric force is greater than 25 volts, or the pressure greater than 0·03$^{\text{mm}}$, proves that the diminution of the current absorbed at low pressures and for smaller electric and large magnetic forces can not be due to the suppression of β- or secondary rays, and must be due to the deflection of the ions.

The adjoining tables contain the currents measured in a number of experiments:

Negative Currents. Electric Force=25 volts c.m.

Magnetic Field.	30$^{\text{mm}}$	15$^{\text{mm}}$	8$^{\text{mm}}$	4$^{\text{mm}}$	1·4$^{\text{mm}}$	·28$^{\text{mm}}$	·06$^{\text{mm}}$
0	·666	·555	·910	·955	2·80	·42	·0503
324	--	--	--	·870	2·33	·058	·0024
567	·625	·513	·800	·835	1·27	·0159	--
1107	·572	·450	·645	·392	·274	·0040	--
1593	·513	·370	·392	·182	·079	--	--
1989	·476	·280	·230	·091	·026	·0022	--
2600	·426	·169	·097	·029	·012	--	--

The first column contains the magnetic field expressed in gauss; and the others the rate at which the potential of the electrode changes expressed in volts per second, this rate being proportional to the ionization current. At the head of each column appears the corresponding pressure of the gas in the ionization chamber, and (for the positive currents) the electric force in volts per centimeter.

The columns are not comparable with each other, for widely different quantities of emanation were used in the different experiments. In order to present more clearly the way in which the currents decrease with increasing magnetic fields, the curves in figs. 3 and 4 have been drawn, taking in each case the current for zero fields as 100.

Positive Currents.

Magnetic Field.	Air 0·002–3mm Electric force=25	Air 0·002–3mm Electric force=10	Hydrogen 0·01mm Electric force=25
0	·0109	·0118	·0280
324	·0104	·0114	·0238
567	·0104	·0114	·0219
1107	·0106	·0111	·0173
1593	·0104	·0105	·0138
1987	·0106	·0089	·0125
2600	·0104	·0077	·0105

An estimate of the order of magnitude of the mass of the ions may be made as follows: Sir J. J. Thomson* has published the theory of ions moving under the action of electric and magnetic forces. In order to apply this theory to the present problem, let the axis of z lie in the plane midway between the two plates and in the direction of the magnetic field H, and let the axis of X be parallel to the elective force X. Thus all the ions will be produced very near the plane yz. Suppose that one of the ions starts from the origin of coördinates at the time $t = 0$, with the initial velocity components w_0, v_0, w_0 parallel to the axes of x, y, z, respectively. According to the theory, at the time t this ion will be found at the point x, y, z given by the equations

$$x = \left(\frac{X}{H} - v_0\right)\frac{1}{\omega}(1 - \cos\omega t) + \frac{w_0}{\omega}\sin\omega t$$

$$y = \frac{w_0}{\omega}(1 - \cos\omega t) + \frac{X}{H}t + \left(v_0 - \frac{X}{H}\right)\frac{1}{\omega}\sin\omega t$$

$$z = w_0 t,$$

where $\omega = \dfrac{He}{m}$.

It appears from these equations that the distances x of the ions from the plane midway between the plates does not increase indefinitely. Its maximum value depends upon the initial velocity and the field strengths, increasing in general as X increases and as H diminishes. If the initial velocity is small compared with the ratio $\frac{X}{H}$, this maximum distance becomes

$$\frac{2mX}{eH^2}$$

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* Conduction of Electricity through Gases, 2d edition, §§ 55–58.

Fig. 3.

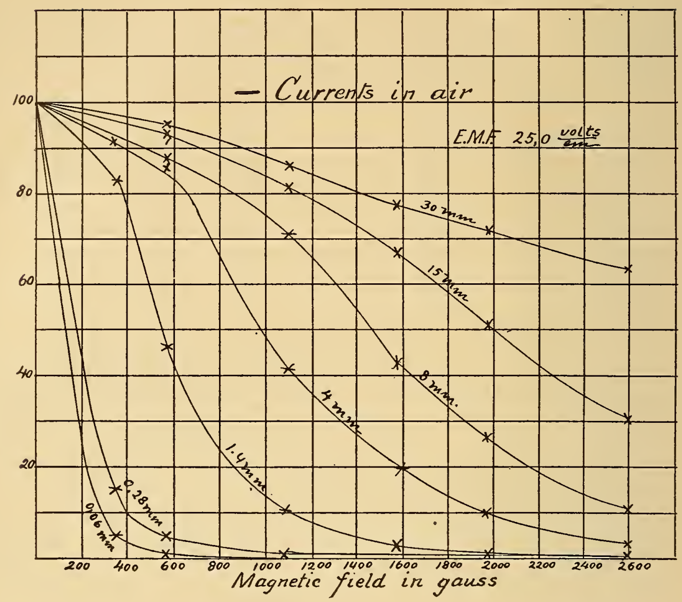
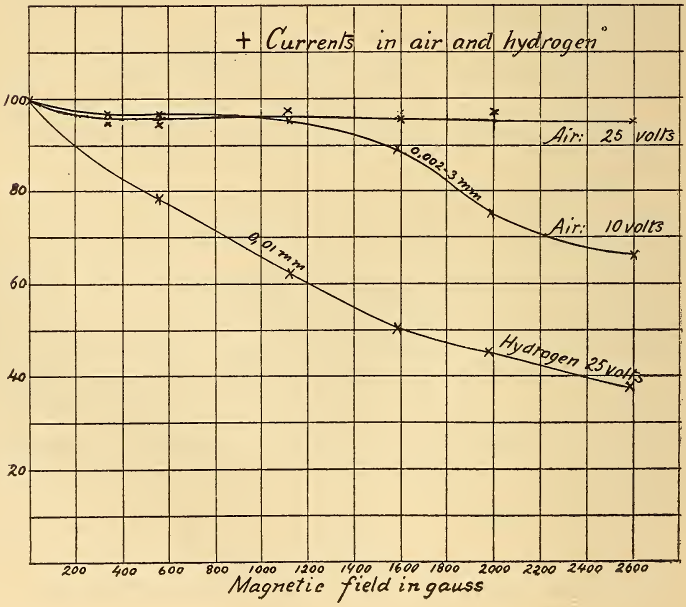

— Currents in air
E.M.F. 25,0 volts/cm
100
80
60
40
20
30 mm
15 mm
8 mm.
4 mm
1.4 mm
0.28 mm
0.06 mm
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
Magnetic field in gauss

Fig. 4.


+ Currents in air and hydrogen
100
80
60
40
20
Air: 25 volts
0.002-3 mm
Air: 10 volts
0,01 mm
Hydrogen 25 volts
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
Magnetic field in gauss

If the ions start with the constant velocity v in all directions from the plane yz the maximum distance they travel from this plane is $\frac{2}{\omega}\left(\frac{X}{H}+v\right)$ and the minimum distance is $\frac{2}{\omega}\left(\frac{X}{H}-v\right)$.

If v is not too large, therefore, we would expect to find that, on keeping X constant and increasing H, the ionization current reaching the electrode would remain constant until the magnetic field approached the value given by the equation

$$d=\frac{2mX}{eH^2}, \tag{1}$$

where $2d$ is the distance between the plates, and that then the current would diminish more or less rapidly to zero. The values of X, H, and d corresponding to the drop in the current strength when substituted in equation (1) should give an estimate of the magnitude of the ratio e/m.

The shape of the curves representing the experiments do not admit of very accurate estimates being made of e/m. The following conclusions, however, may be drawn from the data:

In the first place sensibly all the negative ions at low pressures must have masses of a totally different order of magnitude, and very much smaller than those of the positive ions, even in hydrogen. All the negative ions, therefore, must be corpuscular. This agrees with and extends the results obtained by Townsend,* who used quite a different method, and ionized the gases by X-rays. It is important as showing that *none* of the negative ions are formed by the a-rays splitting up the molecules into positive and negative parts each of molecular dimensions.

Let us apply the theory to the experiment in which the electric force was 25 volts per centimeter, and no effect of the magnetic field of 2600 gauss was observed on the positive current in air. Since all the ions reach the electrode, d in equation (1) must be greater than half the distance between the plates (1^{cm}), and, therefore, substituting $X=2{\cdot}5\times10^9$ and $H=2600$ in equation (1) we find that

$$e/m < 740.$$

Now the ratio of the elementary charge to the mass of the nitrogen atom is about 700, and it follows that within the limits of error of the experiment, none of the positive ions in air can have a mass less than that of the nitrogen atom.†

From the second experiment in air it appears that a considerable number of positive ions are stopped by field strengths

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* Roy. Soc. Proc. A, lxxxv, 25–29, March 14, 1911.

† Compare Sir J. J. Thomson, Phil. Mag., Oct. 1910, Feb. 1911, and Oct. 1912.

around 2000 gauss, if the electric force is 10 volts. Substituting the values in equation (1), putting $d = 1$, we have

$$e/m = 500.$$

The ratio e/m for the nitrogen and oxygen atoms and molecules are approximately 700, 612, 350 and 306, and it follows, therefore, that a large number of the positive ions in air must have masses of the order of magnitude of those of the nitrogen and oxygen atoms and molecules.

The magnetic field suppresses a much larger proportion of the positive current in hydrogen than in air even when the electric force is 25 volts per centimeter, which proves that in hydrogen the ratio e/m for a large number of positive ions must be much greater than 700, and unless the charge is very large, the mass of these ions must be much less than that of the nitrogen atom.

The facts that the drop in the current is not sharply defined and the positive current not completely suppressed may be due to the presence of ions of different masses, or it may be because the initial velocity of the ions is not negligible or that their mean free paths are not long enough. Further experiments with larger electric and magnetic forces, and perhaps at very low temperatures (to reduce the velocity of the molecules), may elucidate these points.

Art. XIII.—*The Index Ellipsoid (Optical Indicatrix) in Petrographic Microscope Work*; by Fred. Eugene Wright.

During the past half century petrologists have given considerable thought and attention to the development of petrographic-microscopic methods with the result that the methods at present available are in general satisfactory and easy of application. The microscope in petrography is simply a useful tool which enables the observer to ascertain certain details about rocks and rock-making minerals that would otherwise escape his attention. The working petrographer observes the different optical phenomena under the microscope and uses them, when properly interpreted, as important diagnostic features. In order that he be able to interpret the phenomena readily and with the least effort, it is essential that the underlying principles be presented in clear and tangible form, as little encumbered with involved geometric conceptions as possible. So far as the writer's experience goes, this can be done best by considering the wave-front normals alone (without reference to the rays) and by using the index ellipsoid (optical indicatrix) to express their special relations in proper form. This view-point, however, has not, apparently, been taken by English and German writers of text-books on petrography, who prefer the historical method of treating the subject and favor, as a result, several old terms and conceptions such as "axes of elasticity," $\mathfrak{a}$, $\mathfrak{b}$, $\mathfrak{c}$, or X, Y, Z, which are superfluous and tend only to burden and confuse the mind of the observer. These expressions are not employed to any extent by French petrologists, whose usage in this respect might well be universally adopted. In the following paragraphs this situation is presented in greater detail and the advantages of the index ellipsoid emphasized.

Light waves on entering a crystal pass within the influence of its crystallographic forces, which are vectorial in character and modify the light waves in a definite manner. To describe in a systematic way the phenomena which are thus produced and to explain them satisfactorily is the object of crystal optics, which is, as its name implies, a border-land subject, requiring for its elucidation two sciences, crystallography and physics. The relations between the optical phenomena observed on a crystal plate and its crystal system are so intimate and fundamental that it is possible to determine, as Brewster was the first to show, the crystal system of the crystal plate from its optical properties alone even though the plate itself be irregularly bounded and afford no outward indication of crystallinity. The determination of a few of the optical constants of the crystal plate is, moreover, usually sufficient for the identification of the mineral from which the plate has been cut; it is for this reason especially that the practical determination of the optical constants of minerals in the thin section is of fundamental importance in petrography.

Experience in crystal optics has taught that a number of different geometrical surfaces are useful in the solution of problems on the propagation of light in crystals. Thus, (1) the index ellipsoid, (2) the ovaloid of normal velocities, (3) the Fresnel ellipsoid, (4) the inverse ovaloid of ray velocities and the higher-order surfaces derived from these ellipsoids and ovaloids, (5) the surface of normal velocities, (6) the index surface, (7) the wave, or ray, surface, and (8) the reciprocal wave surface are cited in treatises on crystal optics. For a given set of conditions experience has taught further that a particular one of the above surfaces is better adapted than any of the others to express clearly the relations which obtain. This has been, in fact, the incentive for the development of so many surfaces and for their detailed treatment in the text-books. They aid in presenting the same subject from different view-points, emphasis in one surface being placed on the wave-front normals, in another on the wave directions, and so forth. These different modes of expression are essential and convenient for the investigator who is working constantly at the subject, but their great variety and yet close similarity renders their use and application difficult for the microscopist, who readily forgets the nice distinctions between them, and is, as a result, often confused and bewildered in his attempt to explain satisfactorily, by their use, the optical phenomena he observes daily in the study of thin sections of rocks. The phenomena of interference in birefracting crystal plates are essentially spacial phenomena, and their description and explanation involve the concepts of tri-dimensional space. Now most observers do not think readily in terms of space, and as a result consider crystal optics an exceedingly complex subject, difficult to master but only too easy to forget unless practised constantly. It is important, therefore, to present the subject as applied to petrographic-microscopic work in a clear, simple manner, and to burden the mind of the observer with as few details as possible.

It has long been felt that, for the explanation of the particular group of phenomena which the petrographer encounters in work with thin rock-sections, a single one of the above surfaces would be adequate and, if adopted consistently, would materially simplify the presentation of this part of crystal optics. The importance of this fact was first realized by

Fletcher, who suggested in his masterly paper on "The Optical Indicatrix and the Transmission of Light in Crystals" the optical indicatrix (index-ellipsoid) as the surface best suited to meet the situation. Fletcher's treatment of the problem is remarkably clear and convincing and his suggestions have been adopted in many of the recent text-books on physical crystallography. Throughout his essay he considers primarily the rays and the ray directions, with only subordinate treatment of the wave-front normals and their derivation from the optical indicatrix.

The ray directions are the paths followed by the light through the crystal; they are, in short, the lines along which the light energy flows and are of fundamental significance in crystal optics. But in petrographic microscope work, the observations are not made within the crystal plate itself and the interest centers chiefly in the phenomena produced, after emergence, by the light waves as a result of the changes which they have experienced during their passage through the crystal. In rock thin-sections the crystal plates are very thin and most of the observations are made in either central or slightly oblique illumination. Under these conditions it is simpler and more direct to consider only the wave-front normals (i. e. directions perpendicular to the wave-fronts) and to leave the rays entirely out of the discussion. This statement does not mean that the significance of rays should be passed over in silence but simply that for the working petrographer the conception of the wave-front normals is sufficient to explain practically all the phenomena which he encounters. The exclusive use of wave-front normals renders, moreover, the application of the optical indicatrix direct and easy to grasp. Although this mode of applying the optical indicatrix is different from that recommended by Fletcher, it seems to the present writer to be better adapted for this particular phase of crystal optics and if employed consistently would do much to facilitate the presentation of microscopical petrography.

For a given mineral the optical indicatrix or index ellipsoid is, in the most general case (biaxial minerals), a triaxial ellipsoid whose principal axes are directly the three principal refractive indices of the mineral for the particular wave length of light employed. Having once obtained this ellipsoid and its position in the crystal relative to the crystallographic axes or other definite directions, it is possible, by its use, to predict quantitatively the optical behavior of any plate cut from the crystal. If the plate be considered to pass through the center of the ellipsoid,* the surface of the ellipsoid intersects the plate in an

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*In any given crystal all plates, cut parallel to a definite plane, have identical vectorial properties; any plane may, therefore, be considered to pass through the center of the index ellipsoid.

ellipse, whose major and minor axes, γ and α, furnish directly the refractive indices and the directions of vibration of those light waves whose front-normals, both before and after incidence, coincide with the normal to the plate. For obliquely incident waves a similar relation exists between the index ellipsoid and the wave-front normals, but the refractions at the surfaces of the plate have to be taken into account and the direction of the resultant wave-front normals within the plate considered; in calculating these directions for rock minerals of medium or weak birefringence it is permissible to use the average refractive index of the mineral and to disregard the rotatory effects of the boundary surfaces on the planes of vibration of the obliquely transmitted waves.

In short, it is possible by means of the index ellipsoid to account, in a systematic and quantitative way, for the various optical phenomena, such as refractive indices, positions of extinction, birefringence, optic axial angle, optical character, direction of elongation, etc., which are encountered by the microscopist in work with mineral plates in monochromatic light. The index ellipsoid is, moreover, different for different wave lengths of light, both in shape and often in position, within the crystal, and these differences find expression in the various color phenomena, such as color, pleochroism, interference colors, dispersion of the bisectrices, and dispersion of the optic axes, which are observed on crystal plates and which are also important diagnostic features.

In view of these facts it would seem logical and feasible to describe and to systematize, on the basis of the index ellipsoid, the optical properties thus made use of in practical mineral determination under the microscope. Thus for a given mineral, the most important optical feature to be ascertained is obviously the type of its index ellipsoid, whether a triaxial ellipsoid, an ellipsoid of rotation or a sphere. In the first case the mineral is biaxial (there are two optic axes, and two axial ratios are required to define the shape of its index ellipsoid); in the second, uniaxial (there is only one optic axis, and one axial ratio is sufficient to define the shape of its index ellipsoid); in the third, isoaxial or isotropic (all axes are equal, and the index ellipsoid is a sphere). This optical feature of the mineral, which defines the shape of its index ellipsoid, has been called the "*optic ellipsoidity*"* of the mineral and is the primary distinguishing characteristic on which the minerals are grouped in the tables given in recent text-books on microscopical petrography.

The most direct method for determining the optic ellipsoidity of a mineral is the measurement of its principal refractive

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* F. E. Wright, Jour. Geology, xx, 488, 1912.

indices on the total refractometer or by use of refractive liquids. The three principal refractive indices establish definitely the shape and size of the optic ellipsoid and with it the principal birefringences, the optic axial angle, and the optical character of the mineral; the optical properties can also be, and usually are, determined by other methods, but they have been purposely listed together to show the fundamental character of the principal refractive indices (the lengths of the principal axes, α, β, γ, of the index ellipsoid). Other methods are also available for ascertaining the optic ellipsoidity of the mineral, but their description would lead too far in the present paper.

Turning to any given section of a birefracting mineral, we find that the optical phenomena which it presents can be adequately described and accounted for when the shape and position of its optic ellipse are known. By determining this feature, the "*optic ellipsity*"* of the section, we ascertain the lengths of the major and minor axes γ' and α', of its optic ellipse (the two refractive indices of the plate); their difference $\gamma'-\alpha'$ (measure of the birefringence); and the positions of extinction of the plate between crossed nicols. These positions are commonly referred to some definite crystallographic direction on the plate, the angle between that direction and one of the axes of the optic ellipse, α' or γ', being called the extinction angle. In German literature these directions are expressed by the symbols $\mathfrak{a}$, $\mathfrak{b}$, $\mathfrak{c}$, the so-called "axes of elasticity," whose lengths are the reciprocals of α, β, γ, the Greek letters being reserved for the refractive indices alone. In this country the symbols X, Y, Z are largely used as a substitute (suggested by Iddings) for the German letters, which are less easy to write. The French, however, use directly the lengths of the optic ellipse α, β, γ (n_p, n_m, n_g), in their expression for extinction angles, and this seems to the writer by far the preferable practice. It can only add confusion to introduce the conceptions of "axes of elasticity." The mechanical theories of light based on an elastic ether have often been called in question and have been largely superseded, since the time of Maxwell, by the electro-magnetic theory. It would seem therefore advisable to drop the terms "axes of elasticity" altogether from petrographic literature, especially as they do not aid but rather detract from the real picture obtained from the use of the index ellipsoid alone, which is valid regardless of the particular theory of light the observer favors. The French method should be consistently adopted and extinction angles expressed in terms of the axes of optic ellipse of the section; thus for diopside the angle of extinction on 010 is $c:\gamma = 39°$, while on

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* F. E. Wright, Jour. Geology, xx, 488, 1912.

110 it is $c : \gamma' = 33°$. In view of the fact that, except in French literature, the Greek letters α, β, γ are used to express the refractive indices. and these letters are easier to write and to pronounce than the French symbols n_p, n_m, n_g, or n_α, n_β, n_γ, it would seem preferable to adopt the Greek letters throughout. No confusion is introduced by using these letters to designate (1) the principal axes of the ellipsoid and (2) to express their actual lengths; this is evident from the French petrographic literature and the occasional usage of α, β, γ in this sense in the literature of other nations. As noted above, the primary purpose of the present paper is to direct attention to this situation and to urge the consistent adoption of this method of expression. From its very nature it is not a matter which can be adopted at once, but it behooves those interested in the development of petrology as a science to make the petrographic microscopic part of the subject as simple and easy of application as possible.

Summary.

In the foregoing paragraphs the importance of presenting the subject of microscopical petrography consistently from the viewpoint of the index ellipsoid as applied to wave-front normals is emphasized. The various optical properties employed in practical petrographic microscopic work can be best described and explained systematically by means of the index ellipsoid. The use of the so-called "axes of elasticity" $\mathfrak{a}$, $\mathfrak{b}$, $\mathfrak{c}$ or X, Y, Z in this connection is confusing and only adds to the difficulties encountered by the observer in mastering the subject. They should accordingly be abandoned and the French usage of naming the principal axes of the index ellipsoid α, β, γ (or n_p, n_m, n_g) adopted. This applies in particular to the different modes now in vogue for expressing extinction angles. For a given crystal face an extinction angle is simply the angle between a definite crystallographic direction on the face and one of the axes, α' or γ', of its optic ellipse, and this fact should be indicated in the expression for the extinction angle. To introduce "axes of elasticity" ($\mathfrak{a}'$, $\mathfrak{c}'$ or X', Z') in this connection is not only needless but less direct, as it introduces entirely new conceptions which experience has shown only tend to bewilder the student. Clear, concise modes of expression and simple methods of attack are as essential in petrology as in other sciences whose development is often directly dependent on the care and attention given by its workers to these features.

Geophysical Laboratory,
Carnegie Institute of Washington,
October, 1912.

Art. XIV.—*The Lava Fountains of Kilauea*; by Frank A. Perret.

The observer, standing upon the brink of Halemaumau, looks down into a pit-crater with the vertical, stratified walls characteristic of the type and with, possibly, a "black ledge" forming a shelf at some distance below the edge and marking a former level of the lava column. If this is still receding, a talus of broken fragments of the ledge—fallen for want of support from below—softens the lower angle, but if, on the contrary, the lava has been rising for some time, the crater floor will extend as an apparently almost flat surface directly to the vertical walls of the pit. In what may be considered the normal state of activity this crater floor consists of a central liquid portion—the lava lake—and a surrounding "shore" of solidified lava chilled by conduction to the crater walls, and growing vertically with the rising lake by overflows from its surface. The liquid portion is maintained at a higher level than the surrounding solid surface by a retaining rim which is formed by accretion during the various oscillatory movements of the constantly agitated liquid and by the spattering of peripheral fountains.

The condition of the crater floor, as it appeared in July, 1911, is shown in fig. 1, and upon the lake may be seen one of the "Floating Islands" to the discussion of which a subsequent paper is to be devoted.

The form of the true crater—as seen when drained of its contents by a subterranean, lateral outflow of lava—is that of a basin over three hundred meters in depth terminating below in a large, well-like opening more than a hundred and twenty meters in diameter, as shown in a sectional design by the survey of E. D. Baldwin in August, 1902.

In times of abnormal activity there is re-fusion of solidified material and a wholly liquid floor (lake) extending to the sides of the pit with a surface practically covered with fountains. Occasionally the lava column fills the basin and overflows into the main crater of Kilauea, thus adding to the flat cone which is gradually filling that greater pit.

Let us now observe the lava lake under normal conditions, as shown in fig. 1. The surface material is moving majestically from some point, often under an overhanging bank where it is rising from below, to one or more localities—it may be at the opposite end of the lake—where it is evidently descending. Under the bank it is seen to be brightly incandescent, but, upon exposure, there forms upon its surface a film of a satiny and often iridescent sheen greatly resembling in appearance the oxidized surface of molten metal in a plumber's solder pot. As the flow is divergent, this skin is pulled apart, forming a series of radiating " bright lines " which, if the activity is moderate, often constitute, at night, the only luminous portion of the surface, exception taken of the fountains. The film gradually thickens by accretion from below and changes from a tough, flexible skin to a true crust which is brittle and cracks under unequal pressure.

Fig. 1.

Fig. 1. Lava Lake, Halemaumau. From east brink, July 1911.

Suddenly a large, circular area of the lake surface, in the center of which a fountain is to appear, is strongly agitated as though a violent up-thrust had been given from below, and in a few seconds there rises through the surface skin a beautiful dome-topped column of perfectly liquid lava—bright orange-yellow in clear sunlight—bursting upward in a shower of fiery drops or boiling, dome-shaped, for a few moments and then subsiding into the lake amid surging waves as the parted surface-lavas close over the spot, where smaller jets continue spouting and a general commotion prevails for some time. Nor even so is the phenomenon at an end, for the cooling of the fountain lava, and the reduction of its volume by contact with air and the loss of its gases, give to it a greater density, and this, together with the acquired momentum of its subsidence, favors rapid sinking and a local void with a lower surface level. The result of this is a general in-surging of surface lava from all sides and a considerable down-flow where the fountain lava sank. In the case of a large fountain appearing at frequent intervals in the same place there may be a practically continuous surging thereto of surface lava whose down-flow will then form a part of the lake's circulatory system. This is especially the case with the peripheral fountains, but the subject of circulation is to be treated specifically in a future paper and this phase is here referred to merely as a direct effect of fountain action.

FIG. 2.

FIG. 2. Telephoto night view. "Old Faithful." Spatter phase.

The noble proportions of the surroundings and the considerable distance from the eye of the observer unite in giving an impression of the size of the fountains which is far below the reality. For visual observation a good glass is essential, but the rapidity of motion renders photography a more satisfactory means of study, providing an image of sufficient size can be obtained with a short exposure. For this purpose the writer employed a Zeiss "Magnar" telephoto equipment having an equivalent focal length of 80^{cm} with a working aperture of F. 10. At an average distance of 200 meters the photographic images of the fountain domes were 5^{cm} in breadth, which gives to the fountains a diameter of fully 12 meters.

The aperture permitted of very short daylight exposures, and at night an exposure of 1/4 second was sufficient, which, if the moment were well chosen, resulted in satisfactory definition.

By this means we distinguish, in the average large fountain, three principal periods which may be designated as, 1, the Spatter Phase (fig. 2); 2, the Dome Phase (figs. 3 and 5); and 3, the Subsidence Phase (fig. 4). Not all the fountains show both the spatter and dome phases, many simply doming up without a drop of lava being thrown off, while others are so scattered that scarcely the semblance of a dome can be observed, but the normal Kilauea fountain shows all three. The spatter phase of these fountains forms the source of the well-known filamentary lava—"Pele's Hair"—the drops thrown from the fountain spinning out glassy threads which are wind-borne to a distance and take the place, as ejectamenta, of the scoriæ, lapilli, and ash of more viscous lavas.

Fig. 3.

Fig. 3. Telephoto night view. "Old Faithful." Dome phase.

When a fountain boils up, bringing highly incandescent lava into contact with the air, the cooling of the surface takes place with extraordinary rapidity, the bright orange dome becoming covered almost instantly with a brown skin which the boiling movement converts into a network of dark lines, as shown in fig. 5. The reader must here be reminded that these lines, as well as the surface skin of the lake, appear lighter in the daylight photograph than the glowing lava of the fountain dome.

Regarding the dynamics of these fountains of lava there has existed a great diversity of opinion. Wm. Lowthian Green*

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* "Vestiges of the Molten Globe," Part II. Honolulu, 1887.

held that the action is purely hydrostatic—the forcing up from below of a simple liquid—and even included in this hypothesis the greater occasional fountains of the Mauna Loa crater, over 4000 meters above sea level. Daly* attributes the phenomenon to the rising of a mass of lava lighter than the rest by reason of greater vesiculation, and which, he says, is " best explained, in part, on the principle illustrated in the upspringing of a log of light wood freed at the bottom of a lake. Through its momentum the log may jump clear out of the lake."

Fig. 4.

Fig. 4. Telephoto night view. "Old Faithful." Subsidence phase.

The present writer goes much farther than this in the direction of a purely gaseous hypothesis, the principal reasons for which are advanced below.

It is, first of all, necessary to realize that, in the active portion of the lake, we have a material which is physically very different from the ordinary conception of lava, and this difference lies principally in its marvellous, its superlative, mobility. Now, that a heavy liquid should be mobile need not cause surprise, as this may be due to its molecular formation — mercury has weight yet it is known as quicksilver. But something more than this is required to account for the mobility of the active lake lava, which is of a different sort to that of mercury, and this is to be found, I believe, in its high gas content. The lava is so charged with gas

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* Reginald A. Daly, "The Nature of Volcanic Action ;" Proc. Amer. Acad. Sci., vol. xlvii, No. 3, June, 1911.

that this is constantly being evolved intermolecularly and expanded upon relief of pressure, and the liquid, while still heavy, acquires some of the peculiarly mobile yet momentum-damping qualities of *foam.* A piece of rock, tumbling over the talus and reaching the shore with just sufficient momentum to topple over into the lake from a height of but a few centimeters, sinks with apparently less resistance than in water and the liquid closes over it without a splash. Daly's quaint statement regarding the flow of pahoehoe* might well, I believe, be applied to this material—it "moves, as it were, on molecular and vesicular 'ball-bearings'."

FIG. 5.

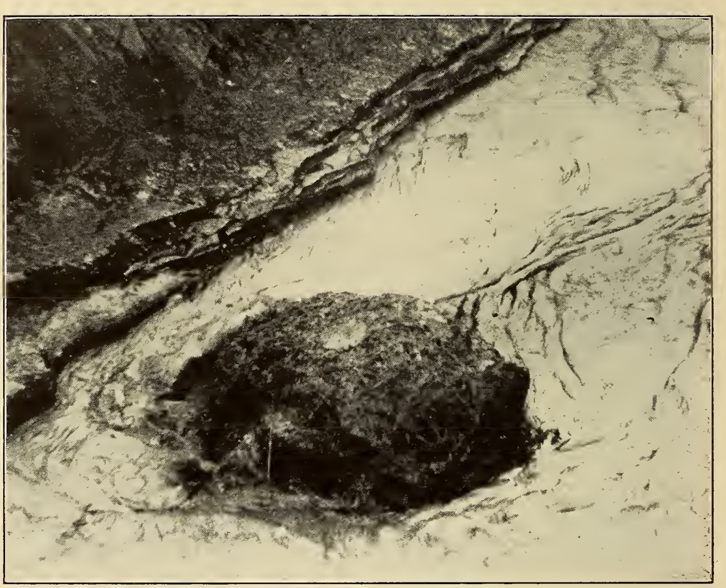

FIG. 5. Telephoto day view. "Old Faithful." Dome phase.

As a result of this condition large gas bubbles may rise rapidly through the liquid and produce fountains, and yet escape without visible commotion—excepting in the spatter phase—other than the boiling movement of the dome, and, as the gas is invisible, many observers have asserted its non-existence. Fortunately, however, an observable phenomenon enables us to prove our contention—the gas, on coming in contact with the atmosphere, *burns.* The flames, which have frequently been

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*Op. cit., p. 108.

seen issuing from spatter cones on the shore or from blow-holes in spatter grottoes at the lake margin, are generally described as having a blue or green color, but we must here guard against effects complementary to the glare of the lava. A stream at Etna emitted vapors which were colorless by day but, as twilight came on, the lava glowed strongly red and the vapors appeared green, while at night their tint was violet against the golden yellow glare.

The flames are faintly luminous and are only visible against a dark background. In fountains with a pronounced spatter phase the flame is lost to sight in the brightness of the scattering drops, but in fountains limited to the dome formation (fig. 3) the flame may always be seen (but not photographed) issuing from the top of the dome as a flash of brief duration. During three months of continuous observation comprising a rising, stationary, and falling lava level, every fountain dome produced its flame, and the many visitors, to whom it was pointed out, had no great difficulty in observing the phenomenon.

Fig. 6.

Fig. 6. Cloud of burnt gases from a lava fountain (seen over ×).

But here again we are fortunate in being able to appeal to the photographic record, for, if the gases which leap from the fountains are invisible by daylight, the products of their combustion are not so, but form a transparent cloud of light blue vapor—also faintly visible—but which, by reason of its highly actinic color, is easily photographed. In fig. 6, above the mark ×, may be seen the round area of a subsiding fountain dome and, over it, the cloud of burnt gases, undisturbed, in this case, by the wind which frequently prevents the photographing of this phase of the gaseous outburst.

The emission of gas is also constantly, if quietly, going on over the entire surface of the lake. With a powerful binocular the writer was able to observe that every one of the innumerable small openings in the crust had its own little blowpipe jet of burning gas. The pressure was high and the jets of flame, inclined in all directions by the obliquity of the holes, were straight, pointed and perfectly motionless. Fissures in the crust produce broad sheets of flame as steady as the pointed jets.

On the subject of the chemical composition of this gas the writer prefers not to enter at present. The research work now being carried on at Kilauea will soon result in the complete analysis of the gases collected over the boiling lava before burning in air, and until this is forthcoming it is advisable to be patient. The present paper is intended to form a contribution to the physical, and not the chemical, study of the lava fountains. It should be stated, however, that, in all my experience with Italian volcanoes, wherever fresh, active lava has first issued into contact with the atmosphere the gases have burned with a flame identical in appearance with those at Kilauea. At Etna in 1910 a continuous jet had a height of from 10 to 20 meters and was blown in all directions by the wind.

But these gases which issue from the liquid lava of a volcano are not, in the writer's opinion, to be considered as juvenile gas in its primal state but that which, expanded into and worked over with the lava in the volcanic edifice, is subjected to the action of air, water and oxidizing and transforming processes of the most complicated kind resulting in the formation of those oxidized and hydrated compounds of sulphur, carbon, chlorine, etc., which constitute the gaseous emanation of ordinary volcanic activity. But the pure magmatic emanation, i. e. the *paroxysmal* gases of a great eruption which, after the expulsion of the liquid lava in the throat of the volcano, issue directly from the depths in a cloud of magmatic ash, are sweet and clean as the air itself and appear to have the same composition. On two occasions at Vesuvius in 1906 and once at Stromboli in 1912 the writer was enveloped in the cloud of gas and ash at distances of from 1500 meters to only 250 meters from the crater during paroxysmal activity. The darkness was absolute from the density of the cloud and the condition continued, in one case, fully twenty minutes; yet, not only was there no difficulty in breathing but no trace of HCl, SO_2, H_2S, etc., could be perceived by one accustomed to detecting these in small amounts.

Returning to the Kilauea lake we see that very small fountains play over all portions of the surface where the resistance of the crust is low, as in the "bright lines." They are evidently caused by the coalescence, below the surface, of small gas vesicles into larger ones with greater tension and ascensional power. This action is automatic and small quantities of the active lava, isolated from the lake, continue to show all its phenomena until liquidity ceases from loss of heat, even the pahoehoe streams which overflow the rim of the lake continuing to show tiny fountains upon their surface until it cools over.

Fig. 7.

Fig. 7. Etna 1910. Permanence of gas sources on flowing lava.

The so-called "travelling fountains" are due to the circulation of the lava, in spite of which three or four large fountains maintain a remarkable constancy of position in the area lying approximately over the Halemaumau conduit, among which the one known as "Old Faithful" is preëminent. It would seem that the gas bubbles, rising through the liquid mass, create a path of less resistance which tends to be perpetuated by further emission. A striking example of this was seen at Etna in 1910, where the loci of the explosions were continued as the stream flowed downward (fig. 7).

The writer holds that the fountains of Kilauea are caused by the rise and expansion of large bubbles of gas in a hypermobile lava. The jets of incandescent, liquid lava at Stromboli, Vesuvius, Etna, etc.,* are true lava fountains in which the spatter phase prevails because of the somewhat greater viscosity of the lava.

That some forms of volcanic action are quiet and non-explosive need not signify that they are non-gaseous. Eruption is, fundamentally, not explosion but emission of gas. Explosion occurs when the emission is obstructed and the gases have acquired sufficient tension to remove the obstruction. The writer believes that the great outpourings of basalt during fissure eruptions were accompanied by the emission of enormous quantities of gas.

Gēite may well be the condensed gas deduced by Arrhenius working up into magma which finally separates out into gas and lava.

Posillipo, Naples,
November 27, 1912.

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* An example may be seen over the crater in fig. 7.

Art. XV.—*Some Interesting New Species of Arthropods from Devonian Strata of Illinois;* by T. E. Savage.

The first species here described is *Lepidocoleus illinoiensis* n. sp., a barnacle from the Clear Creek (upper Oriskany) chert in Union County, Illinois. The specimen is not complete, a piece having been broken from each end. It is of unusually large size, the incomplete fragment measuring 33^{mm} in length. The specimen is preserved in the form of a cast in the chert, but is almost free from the matrix so that the entire length of one side of the fragment and the greater portion of the other side are exposed. The angular dorsal edge and the greater part of the ventral edge can also be seen. There are two vertical rows of imbricating plates, of which 17 can be counted on one side and 13 on the other. It is apparent that several more plates are needed to complete test. The plates alternate in position along an angular line which is considered the dorsal edge, as shown in fig. 2. The plates are gently convex, and overlap for one-half or more of their length. They are oblong in shape, with rounded corners, and are unsymmetrical, the apex being situated at the free end of the dorsal edge. The plates are ornamented with fine, thread-like lines which run parallel with the dorsal border and the free margin to the ventral edge, as shown in fig. 3. The two sides of the specimen are somewhat unequally convex, probably on account of compression which has slightly flattened one side and has caused the plates on the flattened side to overlap those of the other series along their free ventral edges, as seen in fig. 1.

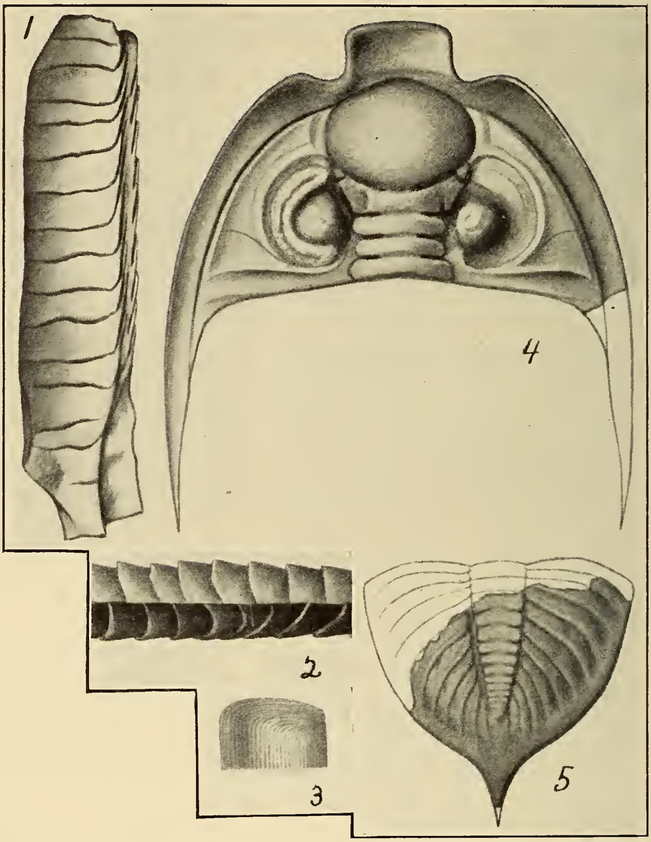
The only known species that approaches this specimen in size is *Lepidocoleus polypetalus*, described by J. M. Clarke from the Helderberg limestone of New York. From the latter our species differs in being somewhat smaller and in tapering less rapidly from below upward. The plates also are less convex and more uniformly curved than those figured by Dr. Clarke.

The other species described in this paper is a trilobite, *Dalmanites palaceus* n. sp., also from Union County, Illinois, where it occurs in strata that correspond in age to some part of the New Scotland formation of New York. The specific name is a Latin adjective signifying shovel-form and was suggested by the shovel-shaped extension at the anterior part of the head.

The head is semi-elliptical in outline to the ends of the genal spines which are directed nearly straight backward and are slightly longer than the glabella. It measures 23^{mm} in length, exclusive of the spines, and 42$^{\mathrm{mm}}$ in width, and is shown in fig. 4.

The glabella is moderately convex, broadest in front, and is bounded by distinct dorsal furrows. The frontal lobe is trans-

FIGS. 1–5.



FIGS. 1–3. *Lepidocoleus illinoiensis* n. sp., p. 149.

1. Lateral view of the specimen showing the overlapping of the plates along the ventral edge, due to compression. × 2 1/7.
2. A portion of the dorsal edge showing the alternating arrangement of the plates on the two sides. × 2 1/7.
3. A single plate showing its asymmetry and ornamentation. × 1 1/2.

FIGS. 4 and 5. *Dalmanites palaceus* n. sp., p. 149.

4. Dorsal surface of an almost complete cephalon. × 1 5/8.
5. Dorsal surface of a pygidium. × 1 5/8.

versely subelliptical in outline, and is slightly more elevated than the lateral lobes; its length is three-fourths of its width and it comprises nearly one-half of the glabella. The first lateral lobes are wedge-shaped in outline and about twice as wide at the dorsal furrow as at their inner extremities. The second lateral lobes are oblong in shape and smaller than the first. The third lateral lobes are similar to the second, but somewhat smaller. The outer extremities of the first lateral furrows are nearly opposite the anterior ends of the eyes, from which they extend obliquely backward and inward. The second pair of lateral furrows are nearly transverse in direction, and are not continuous across the median portion of the glabella. The third pair are similar in direction and extent to the second. The occipital furrow is continuous across the posterior margin of the glabella and meets the dorsal furrow on either side, being deeper on the lateral extremities than over the median portion. The occipital segment is slightly longer and wider than the second and third lateral glabellar lobes, and its anterior and posterior margins are nearly parallel.

The cheeks are nearly triangular in outline, and have a depressed marginal border which continues around the front of the glabella. This marginal depression separates the anterior portion of the glabella from the short shovel-shaped median extension, on either side of which the margin is rather deeply sinuate. The posterior limbs of the facial sutures extend outward and slightly upward from the posterior extremity of the eyes, cutting the lateral margins a little behind a line through the center of the eyes. The eyes are large and crescent-shaped, their length about one-half that of the glabella. The height of the faceted portion is about one-third of their length. The inner side of the eye lobes slope rather steeply to the dorsal furrows. Between the eyes and the marginal furrows the surface of the cheeks is convex. The marginal border is rather broad and is widest toward the front except at the sinuses on the sides of the anterior median extension, where it is narrowed to about one-half its usual width. The posterior cheek furrows extend almost straight outward from the posterior extremity of the eyes to the marginal furrows.

The entire thoracic portion of the species was not seen.

The pygidium is depressed convex, semi-elliptical in outline, and has a width of 22^{mm} which about equals its length inclusive of the flattened caudal spine. The latter measures about 6^{mm} long. The axis is depressed convex and is sharply defined by lateral furrows. At its anterior end the width of the axis is slightly more than one-fourth of the greatest width of the pygidium. It tapers gently posteriorly and terminates in a bluntly rounded end a short distance within the flattened marginal border. It is divided into 14 segments by narrow transverse furrows which are deeper at the sides than over the median portion. The surface of the pleural lobes is gently convex, with a somewhat flattened border. They are divided into about 11 segments which end a short distance from the lateral margins, and become obsolescent posteriorly.

This species closely resembles *Dalmanites tridentiferus*, which was described by Shumard from strata of about the same age on the Missouri side of the river. It is especially distinguished from Shumard's species by having the anterior median extension short and concave, with margin entire, instead of having that extension prolonged into a three-lobed process.

Art. XVI.—*On the Mechanism of the Chlorination of Benzene in the Electrolytic Cell*; by R. G. Van Name and Carlton H. Maryott.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxl.]

As a result of the success attained in the use of electrolytic oxidation and reduction processes in the preparation of organic compounds, attention has been drawn from time to time to the possibility that the development of electrolytic methods of chlorination might yield results of practical value. Thus Nernst* in 1897, in referring to the untried possibilities of such methods, expressed the conviction that it would prove practicable, in the chlorination of organic compounds, to obtain every possible stage of chlorination by varying the electrode potential. Up to the present time, however, the literature upon the subject of electrolytic chlorination and bromination has remained very limited, and, apparently, experimental investigation along these lines has met with indifferent success.

As early as 1852, Riche† obtained monochlor-acetone by electrolysis of a mixture of aqueous hydrochloric acid and acetone, and by a similar method, using hydrobromic acid, prepared monobrom-acetone. These methods were further studied at a much later date by Richard‡. In 1901, Zehrlant,§ by electrolyzing 4-normal hydrobromic acid containing phenol, obtained a twenty per cent yield of bromphenol, and showed moreover that the depolarizing action of the phenol toward bromine produced a marked depression of the anode potential.

Schleuderberg,‖ in 1908, described a series of experiments on the electrolytic chlorination of acetic acid, benzene and toluene. Of the methods tried by him the following gave the best results: Acetic acid saturated with zinc chloride gave a maximum current yield of 12·9 per cent; benzene, dissolved in ether saturated with zinc chloride, yields of 76 and 80 per cent; toluene, mixed with a concentrated aqueous solution of hydrochloric acid and kept at the boiling temperature, yields of 50 to 70 per cent. These current yields are calculated from the total amount of combined chlorine exclusive of chloride, and therefore do not necessarily refer to a single product.

There are obviously two ways in which chlorination may take place in the electrolytic cell; *(a)*, by a strictly electrolytic process, confined to the surface of the anode, as in the case of electrolytic oxidation; or *(b)*, by the secondary action of the dissolved chlorine gas previously set free by the current

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* Ber. xxx, 1547.

† Comp. rend., xlix, 176.

‡ Comp. rend., cxxxiii, 878 (1901).

§ Zeitschr. f. Elektrochem, vii, 501.

‖ Jour. Phys. Chem., xii, 583.

and more or less distributed through the liquid. It is a matter of some importance to distinguish between these two processes. It may happen that *(a)* and *(b)* occur together but give different products, but in any case where the products are the same and process *(b)* predominates, the use of the electric current is for practical purposes entirely superfluous, since the results could be duplicated by the generally more convenient method of treating directly with chlorine gas.

Schleuderberg specifically states his views on this point only in the case of acetic acid, which he places under *(b)*. It seems evident, however, that he regards his chlorination of benzene and toluene as largely of the kind *(a)*, both from the nature of the conclusions drawn from his experiments, and from the fact that the very much lower efficiency observed with acetic acid is cited as the reason for regarding its chlorination as secondary.

The observation of Zehrlant, that phenol may behave as a depolarizer toward bromine, is strong evidence that phenol is capable of entering into a strictly anodic reaction with the halogen. It remains to be determined whether in practice the conditions can be so regulated that the bromination obtained is mainly of this kind.

The evidence for the anodic chlorination of toluene is hardly conclusive, and seems to rest entirely upon a difference observed* in the electrolytic product in the ratio of ring to side chain substitution, as compared with that obtained by direct treatment with chlorine in the absence of a carrier. Still more uncertain is the case of benzene, hitherto investigated only by Schleuderberg. Although, as stated above, Schleuderberg appears to accept the anodic chlorination of benzene as an established fact, it is hard to see how any strong argument in its favor can be based upon his published results alone.

In the present paper it will be shown that the electrolytic chlorination of benzene, at least under the conditions covered by our experiments, is largely and perhaps wholly the result of secondary action. Attention has been confined in our experiments to the effects produced by the electrolysis of a homogeneous solution of benzene together with an inorganic chloride in a non-aqueous solvent. Most of the commoner solvents are excluded by the requirements of the case. We have carried out quantitative measurements with only two, ether and glacial acetic acid. The latter proved far more satisfactory and was employed in all experiments except one preliminary series. Lithium chloride, dehydrated by heating nearly to fusion, was used as electrolyte with acetic acid; anhydrous zinc chloride was employed with ether.

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*Schleuderberg, Jour. Phys. Chem., xii, 598, 1908; Cohen, Dawson and Crossland, Jour. Lond. Chem. Soc., lxxxvii, 1034, 1905. See also comments of Bancroft, Jour. Phys. Chem., xii, 417.

The first point investigated was the influence of changes in the conditions upon the current yield when the above solutions were electrolyzed between electrodes of platinum or of Acheson graphite. Light was excluded from the cell by wrapping with black paper and by other expedients. The total amount of combined chlorine, exclusive of chloride, in the product of each experiment was determined by analysis, and the current yield calculated by taking the ratio of this weight to one half the weight of chlorine equivalent to the number of coulombs used. The coulometer was one of the oxy-hydrogen type and had a graduated gas reservoir of one liter capacity. During the electrolysis the liquid was invariably found to contain free chlorine. Platinum electrodes were always slightly attacked, and at the higher temperatures to such an extent that it was impracticable to use them. Graphite electrodes were not in any case visibly affected. The principal results are recorded in Table I.

TABLE I.

Current, 0·05 to 0·15 amperes. Time, 20 to 36 hours.

Composition of Solution	Number of Exp.	Anode Material	Current Density Amp/dm$_2$	Temperature C	Current Yield %	
Ether, Benzene, equal volumes, saturated with ZnCl$_2$	1.	Platinum	0·10	30°	88	
	2.	"	0·10	25°	65	
Glacial Acetic acid, 5 vols.; Benzene, 4 vols.; Lithium Chloride, 3·5 grams per 100^{cc}	3.	Platinum	0·10	27°	70	
	4.	"	0·05	25°	36	
	5.	"	0·50	25°	51	
	6.	"	0·10	10°	64	
	7.	Graphite	0·10	10°	14	
	8.	"	0·10	70–80°	50	
	9.	"	0·12	28°	32	
	10.	"	0·80	30°	37	
	11.	"	0·10	28°	41	
	12.	Platinum	0·10	30°	51	
					Substitution %	Addition %
	13.	Platinum	0·10	30°	41	6·6
	14.	"	0·10	28°	31	5·5
	15.	Graphite	0·50	30°	31	3·8
	16.	"	0·50	10°	22	3·0
	17.	"	0·10	40°	38	2·0

Ether was used as solvent in the first series of experiments. Both the experimental conditions and the general nature of the results obtained were similar to those in Schleuderberg's experiments with benzene in ether, referred to above. Schleuderberg's method of conducting the analyses* was followed in most cases.

Two serious objections to this procedure soon led us to abandon it. In the first place there is little doubt that the ether is chlorinated to some extent,† which tends to make the current yields too large. Moreover, the presence of the zinc salt was found to interfere seriously with the reduction of the chlorbenzene in the analysis, causing low results. Although these two sources of error act in opposite directions they make the accuracy of the current yields very doubtful. Little confidence can be placed in the numerical values obtained under these conditions, and we have therefore included in the table only two of the ether experiments, as examples.

In the rest of the experiments of Table I glacial acetic acid was used as solvent, with lithium chloride as electrolyte, and the analyses were made with the aid of a new method developed for the purpose and elsewhere described by one of us.‡ In these, and all subsequent determinations of total organic chlorine, the procedure was as follows: The liquid was first treated with an excess of aqueous sulphurous acid to remove free chlorine, and then neutralized with sodium hydroxide. After shaking and standing in a separatory funnel the two layers of liquid were carefully separated, using more water and benzene as required, and the aqueous layer rejected. The upper layer, consisting of benzene containing the chlorbenzenes and a trace of water, was then treated with alcohol and metallic potassium according to the method described in the article just cited, and the chlorine finally weighed as silver chloride. Duplicate analyses so conducted showed close agreement. It will be noticed that if any chlorination of the acetic acid has occurred it will not affect the result, since the chloracetates are removed with the aqueous layer.

Under the conditions of Table I the principal products of the electrolysis are monochlorbenzene and a small amount of benzene hexachloride. The current yields for the first twelve experiments include both addition and substitution chlorine. In the last five both the total chlorine and the addition chlorine

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* Based upon the use of the method of Stephanoff (Berichte, xxxix, 4056, 1906), for determining the organic chlorine.

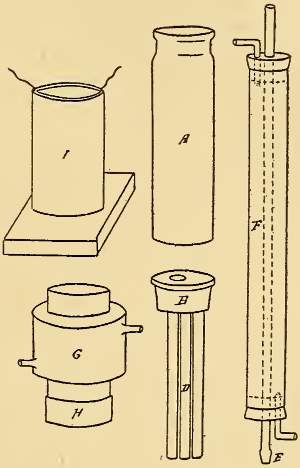
† Two experiments in which no benzene was present, but which in other respects were comparable with experiments 1 and 2 of Table I, showed a chlorination of the ether equivalent to current yields of about 12 per cent and 19 per cent respectively.

‡ This Journal (4), xxx, 378, 1910.

were separately determined, and the substitution chlorine calculated by difference. Addition chlorine, throughout the present investigation, was determined by multiplying by two the weight of chlorine removed by boiling for half an hour with alcoholic potassium hydroxide.

Some trouble was found in constructing a cell available for use at the higher temperatures, since no materials could be used which would not resist the action of chlorine and of the hot vapors of benzene and acetic acid. Figure 1 shows a cell which proved satisfactory and was used in most of the experiments with graphite electrodes. The glass bottle A was 20^{cm} long by 5^{cm} in diameter. The stopper B was made of Acheson graphite carefully ground to an accurate fit in the neck of A, and had in its center a tapered hole into which the lower end of the long glass condenser F was ground to fit. Several rods of graphite D, threaded at the upper end and screwed into the stopper, served as the anode. The cathode, a thin graphite rod, was lowered into the liquid through the condenser by means of a thin platinum wire which supplied the electrical connection. A thermometer was also introduced through the condenser. A double-walled sheet iron jacket G, cooled by circulating water, surrounded the upper part of the bottle, projecting slightly above the stopper, and was attached to the bottle at its lower edge by the heavy rubber band H. The annular space thus left was filled with mercury to a depth of half a centimeter above the top of the stopper, the mercury thus providing both better thermal conductivity and a seal for the two ground joints. Electrical connection with the anode was made through the mercury. Heating, when required, was effected by means of a resistance coil of fine nickel wire imbedded in an asbestos sleeve I, which fitted over the lower half of the bottle.

Fig. 1.



In experiments 1 to 6, and also in 15 and 16, the cathode was enclosed in a narrow, porous cell, but this precaution was omitted in the others after it was found that monochlorbenzene is not appreciably reduced at the cathode.* A slight cathodic reduction of the benzene hexachloride probably occurred when

* See page 169.

no porous cell was used, but on account of the slowness of this reaction[*] and the low concentration of the hexachloride, its effect upon the results must have been very small.

In interpreting the results of Table I the following chlorination experiments, carried out under similar conditions but without electrolysis, are important. A slow current of chlorine gas was passed through the solution for the stated time in the same cell used for the electrolytic experiments (fig. 1), the condenser and all exposed parts of the cell being carefully wrapped in black paper to exclude light.

Exp. 18. Solution: Acetic acid[†] 50^{cc}, benzene 50^{cc}, LiCl about 3·5 grm. Temp. 15°. Time, 24 hours. Yield: Substitution chlorine 1·856 grm., addition chlorine 1·176 grm. (equivalent to 61·3 and 38·7 per cent of the total chlorination, respectively).

Exp. 19. Solution as in Exp. 18. Temp. 80°. Time, 15 hours. Yield: Substitution chlorine 2·939 grm., addition chlorine 0·866 grm. (77·2 and 22·8 per cent).

Exp. 20. Solution: Acetic acid 120^{cc}, LiCl 6 grm., no benzene. Temp. 110°. Time, 24 hours. Yield: 0·370 grm. of chlorine substituted in the acetic acid.

The formation of such considerable amounts of both substitution and addition chlorine in experiments 18 and 19, under conditions where actinic effects must have been negligible, can only be ascribed to the lithium chloride, or to the acetic acid, or to both. A hypothesis which seems to fit these and our later results is that lithium chloride accelerates the substitution process catalytically. Lasarew[‡] has reported a similar effect of the other alkali chlorides.

Experiment 20 shows that acetic acid is also chlorinated in the presence of lithium chloride, though much less readily than benzene.

It is evident from these results that the chlorination observed in the experiments of Table I may have been largely, or perhaps even wholly due to the secondary action of the dissolved chlorine always present in the liquid. The absence of any apparent relation between current density and yield supports this view, and the higher yields obtained with platinum electrodes may well be due to the presence of platinic chloride, which would perhaps act as a chlorine carrier. In short, while these experiments do not disprove, they certainly do not prove the possibility of the electrolytic (anodic) chlorination of benzene. Schleuderberg's results with benzene are equally incon-

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[*] See page 169.

[†] Here, and in all subsequent references to acetic acid, the glacial acid is to be understood.

[‡] J. Russ. Phys. Chem. Soc., xxii, 387 (Ber., xxiii, 546, R.).

clusive, and his results with toluene by no means conclusive, as regards this point.

Anode Potentials.

As a more direct method of attacking this problem, we have employed the well known principle that the presence, about an electrode carrying the current, of a substance having a depolarizing effect, tends to lower the electrode potential. Thus a substance which undergoes true anodic chlorination, i. e. an active depolarizer for chlorine, should produce a measurable lowering of the anode potential, unless its effect is so weak as to be masked by the inevitable change in the nature of the liquid caused by adding the depolarizer.

The measurements were made by the Poggendorf compensation method, with a capillary electrometer. Acetic acid was the solvent and lithium chloride the electrolyte in all cases. To avoid contaminating the solution with water a special reference electrode was used, composed of a silver rod dipping into an approximately normal solution of lithium chloride in acetic acid to which a drop of a water solution of silver nitrate had been added. Except for a short distance at its lower end, the rod was coated with a layer of fused silver chloride to prevent possible disturbing effects at the junction of air, metal, and solution. The potential of this electrode was determined before and after each set of measurements bv comparison with a normal calomel electrode. No appreciable changes in the potential of the silver electrode occurred during the short periods involved, but distinct changes took place upon long standing.

The electrolytic cell was a small glass jar of about 70^{cc} capacity, fitted with a rubber stopper. Anode and cathode were of bright sheet platinum, 21×50^{mm} and 11×25^{mm} respectively, carried by short platinum wires sealed into glass tubes passing through the stopper. The latter was also perforated to admit the bent connecting tube of the vessel containing the silver electrode, whose outlet was placed directly behind the middle of the anode.

After measuring the anode potential in the pure solution of lithium chloride in acetic acid at a given current strength, the benzene was added, the current adjusted to the previous value, and the anode potential again determined. In every case the benzene was found to cause a distinct rise in the potential.

That the benzene, by depressing the ionization of the lithium chloride and thus lowering the concentration of the Cl' ions, would have a tendency to raise the anode potential, would be expected, and the obvious conclusion is, that in practice this effect more than counteracts any tendency which the benzene may possess to lower the anode potential by virtue of its depolarizing power.

A much better test can, however, be obtained by comparing the effect of benzene with that of carbon tetrachloride, a liquid of similar properties, having nearly the same dielectric constant and a viscosity only about 50 per cent greater, but one which, for chemical reasons, would be incapable of acting as a depolarizer for chlorine. The ideal basis for comparison would require that such amounts of the two liquids should be used as would give the same concentration of chlorine ions. In the absence of the data necessary for this adjustment of the proportions, we have employed two different approximations, and have compared the effect on the anode potential of (*a*), equal volumes of the two liquids, and also (*b*), that of volumes which cause like changes in the conductivity. At the dilution employed the effect of 5^{cc} of carbon tetrachloride upon the conductivity was found to be equivalent to that of nearly 6^{cc} of benzene.

TABLE II.

Anode Potentials on Platinum.

	Conductivity at 25°	Anode Potential volts	
	ohm^{-1}	·025 amp.	·050 amp.
Solution A.			
(1·06 *n* LiCl in CH_3COOH)	·00259	----	+1·87
50^{cc} sol. A, 5^{cc} C_6H_6	·00194	----	1·91
50^{cc} sol. A, 5^{cc} CCl_4	·00180	----	1·91
50^{cc} sol. A, 6^{cc} C_6H_6	·00179	----	1·93
Solution B.			
(1·19 *n* LiCl in CH_3COOH)	·00284	+1-66	+1·73
50^{cc} sol. B, 5^{cc} C_6H_6	·00218	1·74	1·80
50^{cc} sol. B, 5^{cc} CCl_4	·00194	1·75	1·79
50^{cc} sol. B, 6^{cc} C_6H_6	·00204	1·89	1·95
Solution C.			
(approx. *n* LiCl in CH_3COOH)	·00242	1·66	1·76
50^{cc} sol. C, 5^{cc} C_6H_6	·00178	1·71	1·83
50^{cc} sol. C, 5^{cc} CCl_4	·00170	1·71	1·82
50^{cc} sol. C, 6^{cc} C_6H_6	·00170	1·71	1·84

Table II shows the results of these measurements. The anode potentials were fairly constant and generally reproducible within five millivolts. The values given have been referred to the calomel electrode as +0·56 volt, neglecting the potentials at the liquid surfaces in the calculations. Although there are discrepancies between the values for the three different lithium chloride solutions, due perhaps to differences in the temperature at which the lithium salt was dehydrated, the general result is the same in each series:—Equal volumes of carbon tetrachloride and of benzene raise the anode potential by almost exactly the same amount, while in proportions giving like conductivities the benzene produces the greater elevation. These facts give no evidence of a depolarizing action on the part of the benzene.

TABLE III.

Anode Potentials on Graphite.

Solution, approximately normal LiCl in CH_3COOH.

	Anode Potential volts	Difference
Solution alone	+1·84	----
50^{cc} of solution + 5^{cc} C_6H_6	1·86	+0·02
Solution alone	1·85	----
50^{cc} of solution + 5^{cc} CCl_4	1·87	+0·02
Solution alone	1·92	----
50^{cc} of solution + 6^{cc} C_6H_6	1·95	+0·03

A like set of measurements with Acheson graphite electrodes, recorded in Table III, gave a similar result, though the effects produced were smaller. The absorptive power of graphite for liquids made it necessary to employ new electrodes for each comparison, but the same lithium chloride solution was used throughout. The variations in the anode potential in the pure solution were largely due to accidental differences in the surface area of different electrodes.

Other Carbon Compounds as Depolarizers.

For comparison with the above results similar experiments were made with a few other substances, including phenol, acetone, ether, and several whose behavior might have a direct bearing upon the problem in hand. These experiments are recorded in Table IV. The platinum electrodes used were those described on page 159.

Phenol produced a marked depression of the anode potential indicating a strong depolarizing action. During the measurement the potential rose rapidly owing to the formation of a thin coating of the reaction products on the anode. When the film was removed and the anode replaced, the initial reading was again obtained but rose rapidly as before. After the electrolysis dilution of the liquid with water gave a precipitate,

TABLE IV.

Other Carbon Compounds as Depolarizers.

Solution, approximately normal LiCl in CH_3COOH (several different solutions used). Current 0·05 ampere.

Depolarizer added to 50^{cc} of sol.	Anode Potential, volts. Before adding depolarizer	Anode Potential, volts. After adding depolarizer
Phenol, 5 grm.	+1·80	+1·69
Acetone, 5^{cc}	1·79	1·78
10^{cc}	1·79	1·75
Ether, 5^{cc}	1·76	1·82
10^{cc}	1·76	1·86
Chlorbenze, 5^{cc}	1·76	1·83
p-Dichlorbenzene, 2 grm.	1·77	1·83
Benzene hexachloride, 2 grm.	1·72	1·76

which was filtered off, dissolved in alkali, and reprecipitated by acidifying. This substance, qualitatively tested, was found to contain a large amount of chlorine, thus confirming the production of chlorphenols in the electrolysis.

In the case of acetone the lowering was small, and may have been due almost entirely to increased ionization, which would be expected here. The depolarizing power of acetone is therefore weak, and perhaps inappreciable.

Ether, and the three chlorine derivatives of benzene, all caused a decided rise in the potential. By itself, this fact is indecisive, but the similarity in the behavior of these four substances to that of carbon tetrachloride is perhaps sufficient to justify the conclusion that no one of them has any very marked depolarizing effect.

Rate of Chlorination with and without Electrolysis.

In these experiments we have measured the rate of chlorination of benzene in a solution kept saturated by a flow of chlorine gas, and contained in a cell through which, from time to time, an electric current was passed. Under these conditions anodic chlorination ought to manifest itself by a more rapid chlorination during the periods of electrolysis. The solution used consisted as before of benzene dissolved in glacial acetic acid containing lithium chloride.

The work was carried out by weak artificial light* in a room carefully screened to exclude daylight, and as a further safeguard the reaction cell was of amber glass. This was a bottle

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* Generally, a single red glass incandescent lamp, but supplemented during the pipetting by a low gas flame.

of about 500^{cc} capacity and 7^{cm} internal diameter, fitted with a rubber stopper carrying the electrodes, thermometer, stirrer, inlet and outlet tubes for the chlorine, and a coiled glass tube for water circulation. The bottle was supported in a thermostat stirred by a motor and kept at the desired temperature, 10°, by means of an automatically regulated flow of cold water. Water from the thermostat was kept circulating through the glass coil above mentioned by a rotary-pump, which helped greatly in maintaining a constant temperature within the cell. The glass stirrer, of the shape obtained by twisting a flat strip into a spiral, was driven by a separate motor. To prevent escape of chlorine from the cell at the point of entrance of the stirrer stem, the latter turned in a trap, made on the principle of the well-known mercury seal, but filled with glacial acetic acid. The electrodes were round rods of Acheson graphite, the anode having a wetted surface of about 40$^{cm^2}$ at the beginning of an experiment, decreasing with the volume of liquid to about 20$^{cm^2}$ at the end.

Chlorine was drawn from a pressure cylinder of the liquid element and washed by passing through acetic acid. Before entering the reaction mixture the gas also passed through a Drechsel bottle supported in the thermostat and containing solution of the same composition as the reaction mixture, thus minimizing the chances of distillation to or from the cell with the gas current.

In beginning an experiment a weighed amount of benzene was diluted to a known volume by means of a solution of lithium chloride and glacial acetic acid, previously saturated with chlorine. A measured volume of this liquid was placed in the cell, the stirrer and gas current started, and the reaction allowed to proceed until the free passage of chlorine showed that saturation was complete. Samples for analysis were then withdrawn from the cell by means of an exhausted bottle into a 10^{cc} pipette with stopcock, from which they were run into aqueous sulphurous acid and analyzed as described on page 156. This process was repeated every two hours. Two samples were always taken for duplicate analyses for total chlorine, and extra samples when addition chlorine was also to be determined. The ratio of addition to substitution chlorine seemed at first to be nearly constant, as observed in a similar instance by Slator,* but our later work proved that in this case the constancy is not complete.

From this ratio and the other results of analysis the loss in concentration of the benzene during each time interval was calculated on the assumption that its products are exclusively monochlorbenzene and benzene hexachloride.† As already

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* Zeitschr. f. physikal. Chemie, xlv, 524, 1903.

† This assumption is supported by the work of Slator, loc. cit.

stated, the method of analysis wholly eliminates the effect of chlorination of the acetic acid from the results.

Since the chlorine concentration was constant the reaction should be of the first order with respect to the benzene, and the velocity constants were, therefore, calculated from the expression $K = \frac{2{\cdot}3}{t_2 - t_1} \ln \frac{a - x_1}{a - x_2}$, in which $a-x_1$ and $a-x_2$ are the concentrations of the benzene at the beginning and end, respectively, of the two-hour time interval.

During every alternate reaction period a constant current (either ·125 or ·200 amp.) was maintained through the cell.

The temperature of experiment, measured in the cell itself, was 10·2°, with a maximum variation at ordinary times of $\pm{\cdot}04°$, but subject to fluctuations of several minutes' duration at the times of starting and stopping the electrolysis. By anticipating these variations by opposite changes in the temperature of the thermostat, they were restricted to a maximum of about $\pm{\cdot}2°$, and their effect reduced by intentionally balancing a low temperature against a high one.

Four experiments were completed, and are recorded in Table V. In all cases $t=0$ is the time when the first samples were taken, i. e. after the saturation with chlorine. Concentrations are all in mols per liter. Experiments 1 to 3 were calculated on the assumption that the ratio of addition to substitution chlorine ($Cl_A : Cl_S$) was constant throughout. In experiment 4 the addition chlorine was determined at the end of

TABLE V.

Experiment 1.

Concentrations: Benzene, initially, 3·7297; at $t=0$, 3·6956; LiCl, 0·85.

Ratio $Cl_A : Cl_S$, 43·9 : 56·1, determined at end.
Electrolysis with 0·125 amp. during periods 1 and 3.

t	AgCl from 10^{cc}		Decrease in conc. of benzene	Conc. of benzene		$k \times 10^4$
min.	grm.	mean	x	$a-x$		
0	·0773 ·0776	0·774	·0341	3·6956		
					Elec.	0·90
120	·1669 ·1671	·1670	·0738	3·6559		
						1·21
240	·2894 ·2827	·2860	·1265	3·6032		
					Elec.	1·58
360	·4408 ·4376	·4392	·1942	3·5355		
						2·08
480	·6357	·6357	·2811	3·4486		

Experiment 2.

Concentrations : Benzene, initially, 1·8777 ; at $t=0$, 1·7633 ; LiCl, 1·07.
Ratio Cl_A : Cl_S, 42·36 : 57·64 (mean of three determinations, 41·6 at $t=0$; 41·8 at $t=360$; and 43·7 at end).
Electrolysis with 0·20 amp. during periods 2 and 4.

$t=$	0		120		240		360		480		600
AgCl, mean,	·2534		·4428		·6406		·8338		1·0183		1·2181
				Elec.				Elec.			
$k\times10^4=$		4·14		4·55		4·70		4·75		5·47	

Experiment 3.

Concentrations : Benzene, initially, 1·8577 ; at $t=0$, 1·8108 ; LiCl, 1·0.
Ratio Cl_A : Cl_S, 41·2 : 58·8, determined at end only.
Electrolysis with 0·20 amp. during periods 2 and 4.

$t=$	0		120		240		360		480		600
AgCl, mean,	·1030		·1824		·2661		·3609		·4310		·5471
				Elec.				Elec.			
$k\times10^4=$		1·69		1·82		2·11		1·59		2·71	

Experiment 4.

Concentrations : Benzene, initially, 1·8161 ; at $t=0$, 1·7872. LiCl, 1·14 ; Chlorine, at end, 1·09.
Electrolysis with 0·20 amp. during periods 2 and 4.

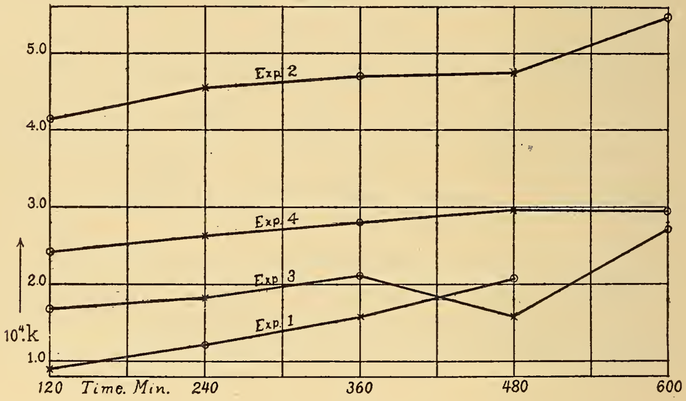
t min.	Total Cl. AgCl from 10^{cc} grm.	mean	Addition Cl. AgCl from 10^{cc} grm.	mean	Percentage of addition chlorine	Decrease in conc. of benzene x		$k\times10^4$
0	·0616	·0616	not	det.	(39·15)	·0289		
								2·42
120	·1708 ·1705	·1706	·0334	·0334	39·15	·0802		
							Elec.	2·62
240	·2847 ·2822	·2835	·0540 ·0559	·0549	38·76	·1339		
								2·80
360	·4061 ·4049	·4055	·0803	·0803	39·60	·1895		
							Elec.	2·97
480	·5256 ·5262	·5259	·1023 ·1047	·1035	39·36	·2466		
								2·95
600	·6501 ·6559	·6530	·1313 ·1343	·1328	40·67	·3012		

each time interval, and the observed values of this ratio used at the corresponding points in the calculations.

The absolute values of the constants in the four experiments differ considerably, owing to differences in the concentrations of lithium chloride and of chlorine, and in the time elapsed between the completion of the saturation with chlorine and the first analysis,* and perhaps also owing to varying amounts of moisture in the reagents used. It is shown by experiment 4, and less clearly by experiment 2, that the ratio $Cl_A : Cl_S$ is not constant throughout the experiment, as assumed in the calculations of Nos. 1–3, but in reality tends to increase. Experiment 4, which is free from this assumption, is consequently the most trustworthy.

Figure 2 shows the constants for the four experiments plotted against the time, constants for the electrolytic periods being designated by crosses, the others by circles. The marked break in the curve for experiment 3 at the fourth constant is doubtless due to accidents in the analysis, since at this point one of the duplicate analyses was affected by a slight loss of material and the other lost altogether. All of the curves have a decided and comparatively steady trend upwards.

Fig. 2.



It is natural to look for the explanation of this rise in reaction velocity in the further chlorination of the primary products. That monochlorbenzene is readily chlorinated under the conditions of the above experiments is proved by the results given in Table VI, obtained by passing, in the dark, a current of chlorine through the solution. The data are insufficient for an exact comparison of the velocity of this reaction with the corresponding value for benzene, but though the former is clearly smaller it is evidently of a similar order of magnitude. It is, therefore, very probable that this reaction is the chief cause of the rise in the benzene constants,

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* In experiment 2 this interval was very long, about three hours, but in the other cases comparatively short.

TABLE VI.

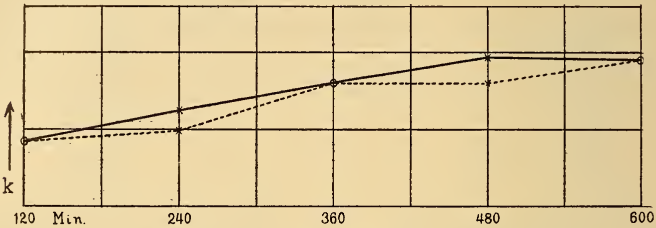
Chlorination in Acetic Acid Solution.

Monochlorbenzene at 10·4° Initial concentrations: C_6H_5Cl, ·147 LiCl, 1·76				p-Dichlorbenzene at 10·4°		
t	AgCl from 10^{cc}		Difference, AgCl	t	AgCl from 10^{cc}	
min.	grm.	mean	grm.	hours	grm.	mean
0	·2178	·2188		0	·2337	·2339
	·2198		·0038		·2341	
180	·2223	·2226		6	·2321	·2318
	·2228		·0062		·2315	
540	·2295	·2288		16	·2325	·2329
	·2282				·2333	

when calculated as above. Table VI also shows that under similar conditions p-dichlorbenzene is not appreciably chlorinated. The rate of chlorination of benzene hexachloride was not tested.

We may now consider whether the results of Table V give any evidence of anodic chlorination. If the chlorination were more rapid during the electrolytic periods it would tend to increase the slope of those sections of the curves in fig. 2 which precede the crosses, and to decrease the slope of those which follow them, thus forming peaks and hollows in regular succession. The results do not confirm this, for the breaks in the curves occur in a wholly unsystematic manner and are in most cases too small in comparison with the errors of experiment to have any weight as evidence of a disturbing effect. It is, however, important to know how large the current yield would have to be, under the conditions, to produce distinct breaks in the direction of the curve. The magnitude of the effect to be expected may be calculated as follows: In experiment 4, period 2, for example, 0·4 ampere hour is equivalent to ·00746 mols of chlorine, which, assuming a 10 per cent current yield, would convert ·000746 mols of benzene into monochlorbenzene. As the volume of liquid was here 300^{cc}, this would decrease the benzene concentration by ·0025 mols per liter. The observed value of x at the end of this period was ·1339, the decrease due to the non-electrolytic reaction, therefore, ·1314. Similarly, at the end of period 4 (volume 230^{cc}), the value of x corrected for a 10 per cent current yield becomes ·2434. If the velocity constants of experiment 4 are now recalculated, using these corrected values of x for the ends of periods 2 and 4, respectively (but not at the beginning of 3 and 5), we obtain the figures given in Table VII, column 5, which represent, subject to the experimental error, the varying velocity at which the non-electrolytic chlorination must have proceeded, upon the hypothesis of a 10 per cent current yield. This is shown graphically in fig. 3, in which the lower (dotted) line connects the values of k calculated in the manner just described, and the black line the values actually observed.

Fig. 3.



A little consideration will show that the deviations of the lower curve from the upper must correspond approximately in nature and magnitude (though opposite in direction) to the effects which the assumed current yield would be expected to produce upon an otherwise constant or uniformly increasing reaction velocity, such as that which the non-electrolytic chlorination would naturally have under the comparatively constant conditions of the experiment. For comparison, the values of k for experiment 4, calculated as above but assuming current yields of 100 per cent and of 5 per cent, are given in the last two columns of Table VII. All these effects would be slightly smaller if in addition to monochlorbenzene the electrolytic reaction yielded any other, more highly chlorinated product, in considerable quantity.

Table VII.

	Conc. of Benzene, $a-x$		$k \times 10^4$		$k \times 10^4$	$k \times 10^4$
t min.	found	10% current yield calc.	found	10% yield calc.	100% yield calc.	5% yield calc.
0	1·7872	1·7872	2·42	2·42	2·42	2·42
120	1·7359	1·7359	2·62	2·49	1·39	2·56
240	1·6822	1·6848	2·80	2·80	2·80	2·80
360	1·6266	1·6266	2·97	2·80	1·27	2·88
480	1·5695	1·5729	2·95	2·95	2·95	2·95
600	1·5149	1·5149				

As a whole, the reaction velocity experiments give no evidence of effects comparable in size or kind to those which, according to the above calculations, a ten per cent current yield would produce. Such effects, if present, could not be wholly masked by experimental errors, and would be plainly evident in the curves of fig. 2. From their absence we may conclude that if electrolytic chlorination played any part in the results, the current yield was below ten per cent.

One other point remains to be considered; the possible influence of cathodic reduction. A test of benzene hexachloride* was carried out by dissolving 3 grams of this substance with 15 grams of sodium acetate in 200^{cc} of acetic acid, and electrolyzing with 0·2 ampere, using the same cell as in the experiments just described. After 14 hours 10^{cc} of the solution gave with silver nitrate ·0058 gram of silver chloride, a current yield of about 1·5 per cent. The reduction is therefore very slow. No reduction of either monochlor- or p-dichlorbenzene was produced under similar conditions.

It is, therefore, probable that a small amount of reduction, affecting only the addition chlorine, actually took place in experiments 1–4. This is confirmed by the fact that in experiment 4 the percentage of addition chlorine shows a slight fall during each electrolytic period. A simple calculation, based on the magnitude of this depression, proves, however, that the effect of the cathode reduction upon the values of the velocity constants was almost negligible and not such as to demand any modification of our previous conclusions.

In the hope of subsequently identifying the principal reaction products, the liquid remaining at the close of experiments 2, 3 and 4 had been in each case shaken with aqueous sulphurous acid and the benzene layer preserved. Fractional distillation of the combined liquids so obtained gave monochlorbenzene, but no certain indication of dichlorbenzene. From the oily residue a small quantity of crystals separated which proved to consist largely of the beta modification of benzene hexachloride. An analysis of 0·04 grm. gave 72·68 per cent of chlorine; theory for $C_6H_6Cl_6$, 73·17 per cent.

Summary.

1. Electrolysis of benzene in a solution of lithium chloride in glacial acetic acid gave chlorinated benzenes with current yields, under favorable conditions, of 50 to 70 per cent. Both addition and substitution chlorine were present in the product, the latter predominating. There was, however, nothing to show that the effects were not due to the secondary action of chlorine previously set free by the current and dissolved in the liquid.

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*The sample used had a melting point of 157° (corr.) and therefore consisted almost exclusively of the *a* form.

2. Benzene dissolved in the same solution is readily chlorinated by direct treatment with chlorine gas in the dark, yielding addition and substitution compounds in proportions which vary with the conditions.

3. The addition of benzene to the acetic acid-lithium chloride solution during electrolysis raised the anode potential, and by an amount equal to or greater than that produced by a similar amount of carbon tetrachloride. This indicates that benzene has little or no depolarizing power toward chlorine, at least in this case. Phenol, added under similar conditions, produced a decided lowering of the anode potential.

4. The rate of chlorination of benzene, when dissolved in the same medium saturated with chlorine, was measured at 10·2°. Simultaneous electrolysis did not accelerate the chlorination perceptibly under conditions where a 10 per cent current yield should have been evident. The current yield, if appreciable, was therefore below 10 per cent.

5. The products of 4 contained addition and substitution chlorine in the ratio of about 2 to 3, this ratio increasing slowly as the reaction progressed. The reaction velocity, calculated on the assumption that monochlorbenzene and benzene hexachloride were the sole products, showed a steady rise, but the rate of chlorination of monochlorbenzene, separately determined, appeared to be sufficient to account for this effect.

6. No positive evidence of strictly electrolytic (i. e. anodic) chlorination of benzene was obtained.

ART. XVII.—*Note on Artificial Sperrylite*; by HORACE L. WELLS.

THROUGH the kindness of the Director of the United States Mint, a specimen of artificial sperrylite has been received by the writer, together with an advance copy of an article relating to it, which is to be published in the forthcoming annual report of the Director of the Mint. The article is by Mr. E. J. Wagor, Superintendent of the San Francisco Mint refinery, who encountered the material and has described and fully identified it. Through the Director's courtesy, also, permission has been given to make use of Mr. Wagor's article in publishing this note.

It may be recalled that sperrylite, which was described* by the writer and examined crystallographically by the late Professor Penfield, has the composition corresponding to $PtAs_2$, that it is the only known natural compound of platinum, and that it occurs in minute, brilliant crystals in the Sudbury region of Canada, in North Carolina, and in Wyoming.

The artificial substance was prepared in the operation of melting anode mud from the electrolytic cells of the copper-refining process. Mr. Wagor says: "This material will probably average 20 per cent to 30 per cent of the precious metals, including 2 per cent to 4 per cent of platinum, with copper in fragments and powder, sulphate of lead, basic sulphates of antimony, bismuth, and tin, sulphides of silver, copper, and iron, arsenates and antimonates, silica, carbon, and fragments of slag. These slimes are washed thoroughly, dried, and melted in crucibles with borax and soda and allowed to settle.

"The crystals were found in a very thin layer of speiss which separated from the metal with considerable difficulty. The fact that the crystals are not attacked by acids generally, and only slightly by aqua regia, led to their discovery in the analysis of the speiss. In washing free from acid, it was noticed that the crystals were not easily wet by water, and notwithstanding their high specific gravity, showed a marked tendency to float when brought to the surface of the water; a marked characteristic of the mineral.

"The microscope develops striking tin-white, isometric crystals with extremely brilliant crystal faces and sharp edges. The crystals are mostly fragmentary, showing cubes, octahedrons and pyritohedrons, and a choncoidal fracture."

Mr. Wagor gives also the behavior of the substance when heated, which is the same as that of the mineral, and he determined the loss by careful ignition in the air, which accounted

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* This Journal, xxxvii, 67, 1889.

for 42·7 per cent of arsenic, and agreed within 0·8 per cent of the theoretical amount.

With the small quantity of the material received, the writer has confirmed its composition qualitatively, and has found that in appearance and pyrognostic properties it agrees precisely with the natural substance.

Professor Wm. E. Ford has kindly established the form of the crystals by the following measurements, obtained from two individuals:

Cube on octahedron, *meas.:* 54° 34′, 54° 49′, 55° 5′ ; *calc.:* 74° 44′.
Cube on pyritohedron (210), *meas.:* 25° 40′, 26° 31′; *calc.:* 26° 34′.
Octahedron on pyritohedron (210), *meas.:* 39° 3′, 39° 31′ ; *calc.:* 39° 14′.

A somewhat remarkable circumstance in connection with the natural and artificial sperrylite is the fact that the crystals are of similar size in both cases. Possibly the artificial crystals may be slightly smaller, on the average, than those of the mineral from the Sudbury region, but the difference is not marked. The natural crystals thus far found have always been very minute—almost microscopic. Since the artificial crystals were prepared on a rather small scale, while the mineral appears to have been formed in massive sulphide ores, such a close agreement in size, as well as in every other respect, would hardly be expected.

While the artificial compound $PtAs_2$ was prepared by the writer by passing arsenic vapor over hot metallic platinum, and the same compound had been made a long time previously by Murray, no distinct crystals were thus formed, so that the new product is of much interest and importance.

Sheffield Laboratory,
New Haven, Conn., November, 1912.

Art. XVIII.—*Dana's Confirmation of Darwin's Theory of Coral Reefs;* by W. M. Davis.

James Dwight Dana, born four years to a day after Darwin on February 12, 1813, naturalist of the United States Exploring Expedition under Wilkes from 1838 to 1842, and afterwards until his death in 1895 professor of geology at Yale University, was for over half a century a leading figure among American men of science. On the hundredth anniversary of his birth, it is fitting to call attention to a contribution that he made many years ago to Darwin's theory of coral reefs, a contribution which has long been overlooked although it supplies the most important confirmatory evidence of the truth of the theory that has ever been brought forward, and at the same time points the way to demonstrate the insufficiency of certain other theories. Dana's contribution consists in his having considered more fully than Darwin did, the changes that must take place in the shore line of the subsiding central island while barrier reefs are developing around it.

Darwin most ingeniously invented the theory of subsidence while he was in South America (in 1835?), before he had seen a true coral reef; he had afterwards only to test the theory by comparing its already deduced consequences with the facts that he observed during the voyage of the "Beagle" across the Pacific and Indian oceans, and with the records of other observant voyagers which he studied carefully after his return to England. The theory bore this test admirably; it explained the things that it was made to explain, and brought into reasonable relationship a large variety of facts that had previously seemed to be arbitrarily distributed. It was therefore regarded as "true" by its inventor; but apart from certain correlations of coral reefs with areas of recent uplift and with active and extinct volcanoes—correlations which appear to be less assured now than seventy years ago—the subsidence theory did not gain that increased probability of correctness which comes from the capacity to explain facts that were unknown or unnoticed at the time of its invention. Nevertheless, for forty years the scientific world accepted it as demonstrated. Darwin's diagrams of a subsiding island and an upgrowing reef have been reproduced over and over again on countless blackboards, as representing one of the great discoveries of geological science.

The introduction of other theories of coral reefs during the last thirty years is familiar matter. Mention will here be made only of a few leading contributions. During the voyage of the "Challenger," Murray saw the reefs of the Fiji islands; he could not explain them by Darwin's theory of subsidence, and he therefore afterwards* replaced that theory by what may be called the theory of outward growth, with its provisos of the organic upbuilding of submarine banks to serve as foundations for atolls, and of the production of lagoons by the removal of the inner part of barrier reefs by solution, no movement of subsidence being included in this theory. Still later, A. Agassiz, in the reports of his world-wide investigation of coral reefs,† emphasized the occurrence of uplifted coralliferous limestones, which might be worn down and dissolved away while new fringing reefs grew around them, thus producing barrier reefs and atolls in association with elevation instead of with subsidence; he suggested further that even volcanic islands might be worn down and obliterated, so that their barrier reefs would survive as atolls. At the same time, he reintroduced the idea of wide sea-cut platforms on the margin of volcanic islands, and the growth of a comparatively thin veneer of coral on the outer edge of the platform, thus producing a barrier reef without subsidence, elevation, or solution. Wharton went farther‡ in suggesting that a volcanic island might be worn down to a depth of 20 or 25 fathoms by marine agencies, thereby producing a submarine bank on which upgrowing corals could form an atoll, and thus, like Agassiz, accounted for atolls without postulating either subsidence, elevation, or solution.

Each of these theories has been more or less favorably received, for each one has the same kind of recommendation as that which sufficed to lead the scientific world to adopt Darwin's theory; that is, each theory explains the group of facts that it was made to explain, provided its postulates are accepted. Such a measure of success is of course commendatory, but it is not sufficient for the establishment of that high degree of probability which is recognized in geological science as demonstration. Even when only a single theory is under consideration, it must evidently do something more than explain the things that it was made to explain, before it deserves unquestioned acceptance. When several theories are advanced to explain a single group of facts and each theory succeeds in explaining what it was made to explain, the need of some independent means of verification is still more manifest. Independent verification of a theory is found usually in one of two ways,

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* Proc. Roy. Soc. Edinb., ix, 1880, 505–518.

† Bull. Mus. Comp. Zool., xxxiii, 1899; Mem. Mus. Comp. Zool., xxviii, 1903.

‡ Nature, iv, 1897, 390–393.

all the better if it is found in both of these ways. New kinds of facts may be discovered after a theory has been invented; if such facts, as well as the original facts, can be reasonably accounted for by the theory, the probability of its correctness is greatly increased. Or new consequences may be deduced from the theory, thus indicating the occurrence of specified kinds of facts not before noticed; if such facts are then found in their designated positions, the probability of correctness of the theory that thus gives its inventor the power of prediction is immensely increased.

The possibility of the development of new atolls by the wearing down of older uplifted atolls, or of new barrier reefs by the wearing down of uplifted older reefs, is one of the interesting complications of the simple theory of subsidence that Darwin touched upon briefly,* but that Agassiz' abundant observations have emphasized. This possibility, however, in no wise affects the origin of the earlier atoll or reef, whatever that may have been. True, Agassiz doubted or denied that the uplifted masses of "Tertiary coralliferous limestone" which he repeatedly found in the Paumotus were atolls of an earlier date, but no other adequate explanation of the origin of these great truncated conical masses, rising several thousand feet over a submarine plateau, has been suggested. Agassiz likewise denied the barrier-reef origin of certain uplifted coralliferous limestones of the Fiji islands, and thus differed from Gardiner,† who on the grounds of his own observations accepted this interpretation of their formation. If the uplifted limestones of the Paumotus and the Fijis are eventually proved to be atolls and barrier reefs of an earlier period than the present, a general theory that explains them will have all the more merit, in that it will then apply to more remote as well as to recent geological time.

Murray's theory of the formation of atolls by upgrowth from submarine banks of proper depth is eminently possible, if the banks can be provided in sufficient number; but possibility is not proof. The depth of the ocean is not supposed to be changed by subsidence in this theory; hence if subsidence is shown to have taken place in the production of barrier reefs, the theory that accounts for neighboring atolls without subsidence will be rendered less probable.

The development of a foundation for atolls by the truncation of a volcanic island in the manner indicated by Wharton is eminently possible, provided no change of level takes place during the progress of the work; but it is inconceivable that floating coral larvæ should abstain from establishing themselves

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* Coral Reefs, 1842, 55, 146.

† Proc. Phil. Soc. Cambridge, ix, 1898, 417–503.

on so good a foundation until the truncation is complete. The ordinary relation of fringing and barrier reefs to their central island suffices to show that the work of marine truncation would be arrested by the growth of reefs, just as soon as the abraded platform became broad enough to afford a foundation for coral growth a moderate distance away from the outwash of fresh water and its detritus; and when such a reef is once established, the further truncation of the island by wave work is practically stopped; the waves of most lagoons are too weak to be effective agents in cutting away the land. Moreover the Alexa bank described by Wharton is as fairly explained by regarding it as a slightly submerged atoll as by taking it for a truncated volcanic island. Hence the theory of truncation, though easily conceivable as to its inorganic elements and received with approval by several writers, involves organic elements which are not admissible. It must be rejected as a means of explaining atolls.

The formation of veneering barrier reefs on the outer margin of submarine platforms cut by the sea around still-standing islands, an old idea* recently given prominence by Agassiz, seems entirely possible, provided that the coral larvæ can be prevented from establishing themselves on the platform soon after its cutting is begun; but the explanation of barrier reefs outside of broad lagoons in this way would involve the same difficulty that is fatal to Wharton's theory. However, if barrier reefs have sometimes been formed in this manner, certain special features should be found in close and constant association with them on the still-standing central island. For after a platform a mile or so in width has been worn by the waves, the central island should rise from the cut-back shore line in a wall of steep cliffs, as Darwin clearly stated,† and the general outline of the cliff-wall should be simplified as compared with the original outline; for marine erosion, after a brief introductory period of increasing irregularity of shore line, tends to decrease the sinuosities of the initial form. If any initial bays existed, due to irregular island-building by volcanic eruption, they should fill with delta plains while the intervening headlands are cut back. The wider the platform becomes, the simpler should be the island outline and the more continuous the cliff wall; but the cliffs should be interrupted here and there by valleys, as long as the area of the island is large enough to maintain streams. After the formation of a barrier reef, deltas should be rapidly built forward from each of these valleys in the quiet and shallow waters of the enclosed lagoon.

Now it may be confidently asserted that the central islands

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* See footnote in Darwin's "Coral Reefs," 1842, 49.

† Coral Reefs, 1842, 49.

of barrier reefs, as represented on large-scale charts, are not as a rule characterized by these systematically associated features. The markedly irregular shore line of Kandavu in the Fiji group, with its many headlands and bays, cannot have been produced by marine action either before or after the barrier reef was formed; and the absence of extensive deltas in the bays discredits the idea of a long still-stand of the island during the cutting of the assumed platform around the headlands in the way postulated in this theory. The platform would be most effectively cut during a period of slow subsidence, provided no coral reefs grew up in the way of the waves; but the essence of this theory lies in the exclusion of subsidence. In the typical barrier reef of Bora Bora in the Society group, the shore line of the central dissected volcanic island is of very irregular pattern, such as marine erosion cannot produce; the sprawling ridges descend gently to their extremities in the lagoon, and are not cut off in cliffs; hence this barrier reef cannot be regarded as a veneer on a wave-cut platform. Moreover, the embayments between the sprawling ridges are little filled with delta plains; hence the island cannot be supposed to have stood still during the long and slow development of the barrier reef by outward growth. The value of wave-cut platforms therefore seems to be limited to narrow examples on which fringing reefs can first establish themselves.

Furthermore, if a veneering barrier reef were uplifted and exposed to normal erosion, it would take the form of a more or less dissected terrace; new-cut ravines would disclose its volcanic structure, the upper surface, strewn with coral sand and silt, would transect the rock structure, and its outer edges might retain patches of the veneering reef. Whether terraces of this kind occur or not may be left to observant explorers to determine.

Murray's theory of outward growth and solution, whereby fringing reefs are converted into barrier reefs during a prolonged still-stand of a volcanic island, is also a manifest possibility; but it involves several consequences, easily deducible from the theory but not usually stated with it. For example, if the central island be several miles in diameter and a thousand or more feet in height, its streams will wash down abundant detritus upon the fringing reef. By the time the reef has grown outwards far enough to be called a barrier, the stream-borne detritus will have formed deltas fronting the mouth of each valley; and with farther outgrowth of the reef the deltas will become laterally confluent, so as to form a low alluvial plain around the original shore line of the island; and this original shore line should not exhibit sinuosities of the kind that are produced by subsidence.

Moreover, the structure of the reef should show cross-bedding on a gigantic scale, for the reef advances on a foundation of its own talus; and in the inclined layers of the talus disordered structures might be locally expected, as the result of submarine "landslides," if they may be so called. During the outgrowth of the reef its superficial parts will be more or less dissolved away in the excavation of the lagoon; hence if such a reef is uplifted, so as to form a terrace around its mountain center, its stratification will be inclined at a significantly steeper angle than the slope of the foundation on which it is built; while in the case of a reef formed during subsidence a large part of the reef may consist of horizontal strata.

The first of these deduced consequences of the theory of outward growth is rarely if ever confirmed by the facts. Existing barrier reefs are not as a rule associated with alluvial plains around the inner border of their lagoons. Delta-plains of moderate extent often occupy the bay heads, but the very form of the bays upon which they encroach shows that subsidence has taken place; and the small area of many delta-plains indicates that the subsidence has occurred during the formation of the barrier reef. Hence the theory of outward growth during a still-stand of a central island is not acceptable as a means of accounting for reefs of this class. The theory cannot be accepted as explaining actual barrier reefs, unless by way of exception, however reasonable it is and however easily it may be conceived.

The second deduced consequence of the theory of outward growth appears to be seldom supported by the facts, for the strata of uplifted reefs, as far as I have read, are usually horizontal. This consequence may perhaps be supported in a few cases, where uplifted reefs are described as possessing inclined strata; but the descriptions of these cases do not suffice to distinguish reefs of outward growth on a still-standing foundation, where the whole reef should consist of inclined strata, from reefs of upward growth during subsidence, where only the peripheral strata should be inclined and the rest horizontal. In several articles in which uplifted reefs are described, the attitude of their stratification is not mentioned; perhaps because it could not be recognized; perhaps because districts of recent elevation have not often in the past offered favorable conditions for the development of thick reefs in which, after elevation, the lines of structure could be easily detected. But the real difficulty here seems to be rather that the observers of uplifted reefs did not have the alternative theories of reef formation and their contrasted consequences clearly in mind; and the records made by such observers are often wanting in critical value. For example, on Eua island of the Tonga group, Lister has described a limestone terrace which he regarded as an uplifted barrier reef; his text is silent as to the attitude of its strata, but his sections show them horizontal. Gardiner describes* the interbedding of washed volcanic detritus with horizontal limestones in an uplifted reef on Viti Levu of the Fiji group, but the context does not make clear the relation in which these alternating strata stand to the foundation on or against which they were deposited. Andrews describes† with considerable detail some of the uplifted limestones on certain members of the Fiji group, but he often fails to mention the attitude of the limestone and "soapstone" layers in masses which he describes as stratified, and his cross-sections cannot be safely utilized because it is impossible for the reader to separate observed from inferred structures.‡ This brief review would seem to indicate that, for the present, no safe decision can be made for or against the theory of outward growth on the evidence of uplifted reefs, because their structure is too imperfectly known.

Two other points deserve mention in this connection. First, the theory of outward growth is not an alternative that excludes the theory of upward growth; the two processes can go on together or alternately. Second, Darwin fully recognized this possibility: he accepted outward growth without subsidence for a reef three miles wide, in which the ridges earliest formed at the back of the reef stand at the same height as those last formed in the front;§ in another case he keenly decides in favor of a stationary period after subsidence because of "the broad belt of low land at the foot of the mountains" (128), while in a third he concludes in favor of upward growth during subsidence, because of "the small quantity of low alluvial land at the foot of the mountains" (128). He concluded that "subsidence supervening after long intervals of rest . . . probably is the ordinary coarse of events" (130); also, that a reef "could not increase outwards, without a nearly equal addition to every part of the slope . . . and this would require a large amount of sediment" (74).

It would thus appear that the outgrowth theory of Murray and the truncation theory of Wharton and Agassiz, when tested by certain consequences that have not been explicitly stated by their inventors, fail to satisfy the requirements of observation. They must, therefore, be either modified or discarded. It remains to be seen whether Darwin's theory of subsidence must suffer the same fate when tested in the same manner.

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* Quart. Journ. Geol. Soc., xlvii, 1891, 500–607; see p. 600.

† Proc. Camb. Phil. Soc., ix, 1898, 417, 503; see p. 454.

‡ Bull. Mus. Comp. Zool., xxxviii, 1900, 1–50.

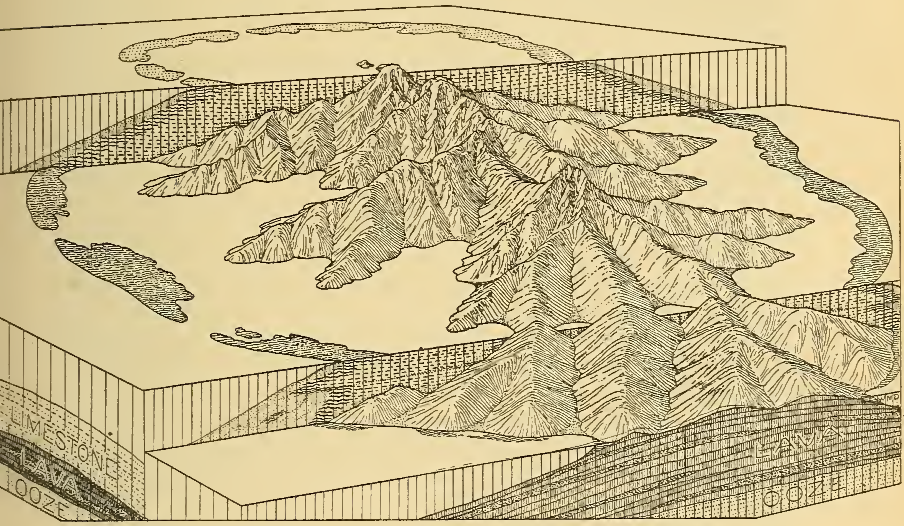
§ Coral Reefs, 1842, 74, 75.

The diagrams by which Darwin illustrated the consequences of his theory are simple transverse sections, and as such they do not sufficiently represent the deductive side of the problem. If they be transformed into block diagrams, in which surface and section are both exhibited, their value in this respect is increased; for, as Passarge has pointed out, block diagrams show what an author thinks rather than what he sees; indeed, it may be claimed for them that they help their author to think, even compel him to think. Therein lies half their value; while the other half lies in the ease with which the reader can, with their aid, understand the thought of the author.

The accompanying block diagram exhibits three stages in the subsidence of a dissected volcanic island: for convenience of drawing, the island is represented as standing still while the ocean rises. In the first stage, a discontinuous fringing reef has been formed; its relation to the island and to sea level is shown in section on the front face of the first block. The second block shows a later stage; the size of the island has now been much diminished by subsidence, and the volume of the reef has been correspondingly increased in its transformation from fringing into barrier position; the inferred horizontal and slanting structure of the reef, with abundant volcanic detritus in the landward part of its horizontal strata, is shown in the front face of the second block: an assumed but unessential pause in subsidence is there indicated by a temporary turn in the reef from upward to outward growth; at the level thus defined, a thin wedge of far-advancing delta deposits is intercalated in all the embayments between the earlier and later calcareous strata of the lagoon, and below this level the thickness of the outer slanting layers is increased. The proportion of inner or lagoon strata, lying horizontal, to the outer talus deposits, lying at a strong angle, may be varied within reasonable limits. For example, in the front face of the third block, where the central island has nearly disappeared, the up-growing reef is represented as of decreasing perimeter, with correspondingly small external talus, thus following Darwin's original diagram. But the most significant feature is yet to be mentioned, although the diagram has probably already suggested it. Darwin recognized the diminishing size and final disappearance of the subsiding island as an essential consequence of his theory: but another equally essential consequence, of which no mention appears in his writings, is the transformation of the relatively simple shore line of the initial island into an indented shore line, as the sea enters the valleys between the ridges of the dissected and subsiding island-mass. As long as subsidence continues, no large deltas can be built forward in the bays by the decreasing streams, no strong cliffs can be cut in the ridge-ends by the relatively quiet lagoon waters. Here are several consequences of the theory of subsidence which were entirely unsuspected by its inventor. If they are matched by the facts, the theory from which consequences so significant and so specific can be deduced will gain a greatly increased probability of correctness.

It requires only a brief examination of large-scale charts of the Pacific island-groups to discover that the central islands within barrier reefs are repeatedly characterized by irregularly embayed shore lines, that the bays seldom contain extensive deltas, and that the ridge-ends are not strongly cut off in cliffs. Kandavu and Mbengha in the Fiji group (Admiralty chart 167), the western members of the Society group (chart 1060) and especially Bora Bora (chart 1428), Gambier island, a western member of the Paumotu group (chart 1112), and Rossel island (chart 1473) in the Louisiade archipelago of British New Guinea, may be instanced among many others as affording good illustration of at least some of these significant features, particularly of embayed shore lines. Furthermore, various uplifted reefs already mentioned are described as having horizontal structure; and Gardiner even mentions, as above stated, beds of volcanic detritus interbedded with the coralliferous limestones in one of the Fiji elevated reefs.

Fig. 1.



Now, in view of the remarkable accordance that is thus found between several peculiar consequences of the theory of subsidence and several features of the central islands in barrier reefs, and in memory of the failure of certain consequences of the theories of outward growth and of sea-cut platforms to match observed facts, an open-minded inquirer cannot hesitate in making choice among the several explanations that have been suggested for barrier reefs, and with them of atolls. We cannot now, as Guppy did,* "pass over the theory of subsidence because the more recent facts concerning the ocean depths and the regions of living and upraised reefs compel us to regard it as no longer necessary." In view of the peculiar features of the central islands of barrier reefs, the theory of subsidence is to-day as valid as it ever was. Indeed, after one has fully appreciated the value that attaches to a successful confrontation of unexpectedly deduced consequences with previously unobserved facts in the verification of a theory from which such consequences have been derived, it is difficult to refrain from giving full acceptance to Darwin's theory, notwithstanding the doubts that have been raised against its sufficiency by more recent investigators. But nothing is gained by over-hasty confidence in a good case. Before one adopts a final conclusion as to the origin of certain reefs, the evidently desirable thing would be to have the whole problem examined again in the Pacific by an investigator who should impartially bear in mind all the theories and all their consequences.

In the meantime, however, I desire to emphasize the point that it is to Dana that we owe the discriminating test above mentioned, which may be applied to the several theories that have been proposed to account for coral reefs, particularly for barrier reefs; for it was Dana who first directed careful attention to the features that ought to be expected on a subsiding central island as a means of testing the theory of subsidence, and hence o other theories also.

Dana first learned of Darwin's theory when the Wilkes Expedition reached Sydney near the end of 1839. It was several months earlier, during "the ascent of Mt. Aorai on Tahiti, in September of 1839," that he first conceived the production of an embayed shore line as a necessary result of the subsidence of a dissected land-mass. "Sunk to any level above that of five hundred feet, the erosion-made valleys of Tahiti would become deep bays, and above that of one thousand feet, fiord-like bays, with the ridges spreading in the water like spider's legs." It is important to notice that this principle, simple as

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* Victoria Inst., 1888, 1–16; see p. 6.

it is, had no place in geology or geography at the time of Dana's voyage. He appears to have been the first fully to recognize, and he was surely the first to state with emphasis, the simple origin of the alternating bays and headlands in an irregular shore line by the partial submergence of a dissected land-mass. He may have been preceded a few years in the general recognition of the idea by De la Beche, who in his "Researches in Theoretical Geology" (London, 1834) states that, on the island of Corsica, "the west coast plunges suddenly into the sea, and the valleys are continued beneath it, presenting numerous inlets where the level of the sea meets the inclined bottom of the valley" (p. 193): De la Beche's attention was, however, given chiefly to the submarine part of the valleys, and only incidentally to the associated outline of the coast. No one, I believe, has hitherto quoted the above sentence in this connection: in Penck's thorough review of coastal forms in his "Morphologie der Erdoberfläche" (Stuttgart, 1894), reference is made to De la Beche's discussion of submerged valleys, but Dana is named as the first to recognize the origin of bays by submergence (582).

Dana, on the other hand, explicitly and repeatedly emphasizes the effect of subsidence in producing bays, and as repeatedly adduces indented shore lines in confirmation of Darwin's theory of coral reefs. In his first report he says,* when explaining the consequences of subsidence: "The very features of the land, the deep indentations, are sufficient evidence of subsidence to one who has studied the character of the Pacific islands," and in a footnote he refers to a later chapter where the following explicit statement is made, under the general heading, "Evidence of subsidence," and the special heading, "Deep bay-indentations in coasts as the terminations of valleys": "In the remarks upon the valleys of the Pacific islands, it has been shown that they were in general formed by the waters of the land, unaided by the sea; that the sea tends only to level off the coast, or give it an even outline. When, therefore, we find the several valleys continued on beneath the sea, and their enclosing ridges standing out in long narrow points, there is reason to expect that the island has subsided after the formation of the valleys. For such an island as Tahiti could not subside even a few scores of feet without changing the even outline into one of deep coves or bays, the ridges projecting out to sea on every side. . . . The absence of such coves, on the contrary, is evidence that any subsidence which has taken place has been comparatively small in amount" (393). A similar statement is made in Dana's first

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*Geology, U. S. Expl. Exped., 1849, 131.

book on this subject, "On Coral Reefs and Islands,"* and in the several editions of his larger book, "Corals and Coral Islands."†

It is singular how seldom the value of Dana's significant evidence has until recent years been appreciated by other students of coral reefs. It is inconspicuously referred to in the appendix to the third edition of Darwin's "Coral Reefs" (London, 1889), prepared by Bonney, who says in this connection that fiord-like indentations in the rocky coasts of islands are "generally admitted to be one of the strongest evidences of subsidence all the world over" (310–311), but the editor does not draw special attention to this evidence as affording an independent and therefore highly valuable confirmation of Darwin's theory. Dana's statement is noted by Krämer,‡ who gives it local application in explaining certain bays of the Samoan islands, but he fails to recognize its general value in relation to the subsidence theory of coral reefs. It is quoted by Gardiner,§ but without recognition of its importance, for he says: "Such evidence when applied to volcanic islands is, I submit, of very doubtful value." Murray does not mention Dana's evidence; Agassiz rejects it, for he writes: "There are . . . no indications that either the Marquesas or Mehetia has been subjected to the effects of subsidence, as Dana assumes."‖ Dana's statement in this connection was: "The Marquesas are remarkable for their abrupt shores, often inaccessible cliffs, and deep bays. The absence of gentle slopes along the shores, their angular features, abrupt soundings close alongside of the island, and deep indentations, all bear evidence of subsidence to some extent; for their features are very similar to those which Kaui or Tahiti would present, if buried half its height in the sea, leaving only the sharper ridges and peaks out of water."¶ Evidently, then, the importance of Dana's contribution to Darwin's theory has been slow in gaining general recognition. This is probably because an understanding of the reasonable evolution of coastal forms has not yet gained general possession of the scientific mind; or perhaps because some students of the coral reef problem still adhere to the obsolete explanation of bays by marine erosion, an explanation which Dana explicitly excluded; can the delay in application of Dana's principle to the coral reef problem be because there is as yet no sufficiently general understanding of the principle

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* New York, 1853, 118–119. † New York, 1872, 319–320, and 1890, 273–274.

‡ Bau der Korallenriffe, Leipzig, 1897, 24.

§ Proc. Camb. Phil. Soc., ix, 1898, 490.

‖ "Coral Reefs of the Tropical Pacific," Mem. Mus. Comp. Zool., 1903, xxviii, 5.

¶ "Coral Reefs and Islands," New York, 1853, 122; "Corals and Coral Islands," New York, 1872, 325.

that a theory, even if it is well recommended by explaining the things it was invented to explain, still needs confirmation by independent and unexpected evidence before it deserves to be accepted as "demonstrated"?

But the most curious feature in all this discussion is that Darwin himself did not announce in the second edition of his "Coral Reefs," Dana's confirmatory evidence of the theory of subsidence that had been published in the first edition of this famous book. Darwin was so open-minded, so fair-minded, so scrupulously careful in considering all sides of a problem, that his failure to bring forward Dana's evidence can only mean that he did not understand it. This is the more remarkable when one re-reads his "Coral Reefs" attentively, and notes the critical and impartial consideration that he gave, not only to his own theory of subsidence but to various other theories, and the thoroughness with which he deduced their consequences for confrontation with the facts. He examined the volcanic crater theory of atolls and dismissed it because it seemed "improbable that there should have existed as many craters of immense size crowded together beneath the sea, as there are now in some parts atolls. . . Nevertheless," he adds, "if the rim of a crater afforded a basis at the proper depth, I am far from denying that a reef like a perfectly characterized atoll might not be formed; some such, perhaps, now exist."* Agassiz reports reefs of this kind in the eastern archipelago of the Fiji group. Darwin carefully considered the submarine bank theory and recognized a certain value in it; he wrote, if "corals were to grow up from a bank with a level surface some fathoms submerged, having steep sides and being situated in a deep sea, a reef not to be distinguished from an atoll might be formed; I believe some such exist in the West Indies. But a difficulty of the same kind with that affecting the crater theory renders . . . this view inapplicable to the greater number of atolls" (89; also 55). Even the newer information adduced by Murray as to the shower of organic material that falls on the sea floor has not altogether relieved this difficulty. Darwin explicitly, though briefly, considered complicated cases of elevation succeeding subsidence, and of subsidence succeeding elevation (140, 145); he recognizes such complications as interruptions in subsidence: "At the Society archipelago . . . the shoalness of the lagoon channels . . . and the broad belt of low land at the foot of the mountains indicate that, although there must have been great subsidence to have produced the barrier reefs, there has since elapsed a long stationary period" (128). He makes repeated mention of uplifted reefs of various kinds, and considers in some detail

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* "Coral Reefs," 1842, 89.

the subsequent degradation of an uplifted fringing reef; the margin of such a reef "would generally during a slow rise of the land be either partially or entirely worn down to that level at which corals could renew their growth on its upper edge. On some parts of the coast-land of Mauritius there are little hillocks of coral rock, which are either the last remnants of a continuous reef, or of low islets formed on it" (55). It is but a step from this case to that of the uplifted and worn-down atolls, which later exploration has brought to light, but the failure to recognize the action of solution made this step difficult: "the supposition . . . that the upraised parts [of atolls] have been worn down by the surf, and thus have escaped observation, is overruled by the considerable depth of the lagoons of all the larger atolls; for this could not have been the case if they had suffered repeated elevation and abrasion" (146). Darwin attentively examined the possibility of the outward growth of reefs from a still-standing foundation, and, although he overlooked the process of solution in forming a lagoon, accepted this process, as above indicated, for certain special cases (52, 75), but rejected it for most barrier reefs, presumably because they show only a "small quantity of low alluvial land at the foot of the mountains" (128; also, 43–45); possibly also because of the extravagantly large amount of coral waste that outward growth demands in the formation of a reef of increasing perimeter in water of great depth, in comparison with the economy of coral waste in a reef, the perimeter of which decreases as the depth of the sea is increased (74, 101). If he did not recognize the possible value of solution in the formation of lagoons, he did explicitly mention the movement of water "thrown over the outer edge" of a reef; "the current thus produced would tend to prevent the channel being filled up with sediment, and might even deepen it under certain circumstances" (54; also 45). He concisely stated the unanswerable objection to the theory of veneering barrier reefs on wave-cut platforms, which had been suggested for the Society Islands even in his time: "It will, perhaps, occur to some that the actual reefs formed of coral are not of great thickness, but that before their first growth the coasts of these encircled islands were deeply eaten into, and a broad but shallow submarine ledge thus left, on the edge of which the coral grew; but if this had been the case, the shore would have been invariably bounded by lofty cliffs, and not have sloped down to the lagoon channel, as it does in many instances" (48, 49).

And yet this most able and impartial investigator, who so logically deduced many consequences from all the theories of coral reefs that had been invented in his time, failed to go one step farther, and to deduce the effect of subsidence in producing an embayed shore line on a dissected island. He must surely have read Dana's paragraph on this point. Indeed, in describing the Marquesas Islands, he says: "Dana infers . . . from their steepness and deeply indented outline, that they have subsided"; * but the general principle here involved did not engage his attention. Even the explicit reference to Gambier Island, a western member of the Paumotu group, in Dana's report† as exhibiting forms that are indicative of subsidence, independent of the occurrence of its well-developed barrier reef, seems entirely to have escaped his notice. How regrettable it is that the great naturalist lost the pleasure of appreciating the value which this evidence possesses in giving independent confirmation to his theory!

In recent years several students of coral islands have, especially in Australasia, given to the evidence afforded by drowned valleys the importance that it deserves. The latest of these is Marshall, of Otago, New Zealand, who writes as follows in his recent essay entitled "Oceania," in the "Handbücher der Regionalen Geologie": "The deep inlets that intersect the coast line of . . . [several islands of the Society group] are clearly due to stream erosion. Prolonged marine action would have shallowed or filled them up or at least would have built up bars of coastal debris across the entrances. The author is therefore strongly of opinion that the absence of cliffs at the termination of the radiating spurs, the presence of deep water in the lagoon, and of far-reaching inlets prove that marine erosion has not had any influence on the form of these islands at the present sea level . . . Finally the deep inlets appear to be drowned stream valleys and their nature strongly supports the belief that the islands have been subjected to an important movement of subsidence."‡ His conclusion is: "The author's observations on the islands of the Cook and Society groups cause him to support Darwin's theory as perfectly full and sufficient to account for the reef phenomena in those islands."§ "Darwin's theory still holds good in the majority if not in all coral areas."‖ This direct testimony from an observer in the antipodes is most welcome. It reaches me through a friend since the writing of this article was begun, and is most apposite in providing precisely that impartial revision of the problem by an open-minded investigator which was pointed out above as desirable before any final conclusion should be adopted. In view of the result of this expert and first-hand investigation, further delay

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* Coral Reefs, 2d ed., London, 1874, 201; also, 163.

† Geology, U. S. Explor. Exped., 1849, 131.

‡ Vol. vi, Sec. 2, No. 9, 1911, p. 13.

§ Ibid, p. 7.

‖ Ibid, p. 30.

in reaching a decision seems hardly necessary. The alternative theories of outward growth on still-standing islands, of veneering barrier reefs on sea-cut platforms, and of upward growth on up-built submarine banks, certainly deserve to be considered wherever they can find application. The down-wearing of uplifted reefs and atolls is evidently pertinent in certain cases of complicated history. Every case must, as Agassiz repeatedly insisted, be independently investigated. Nevertheless, it may now be fairly said that the theory of subsidence deserves for a number of well studied examples the acceptance that it long enjoyed, and that it for a time and in part lost. It affords not merely a possible explanation; it exposes a well-supported explanation of many barrier reefs, and hence probably also of many atolls. The postulate of subsidence, on which Darwin's theory is based, is justified and established by the independent evidence brought forward by Dana.

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *The Isomer of the Potassium Ferricyanide.*—About 13 years ago, Locke and Edwards, working in the Sheffield Chemical Laboratory, described potassium β-ferricyanide, which they prepared by boiling solutions of the ordinary salt with hydrochloric acid. The new salt differs from the ordinary one in crystalline habit, in color, in having a molecule of water of crystallization, and in various reactions with solutions of the heavy metals, the reaction with a dilute nitric acid solution of bismuth nitrate being particularly characteristic, as it gives no precipitate with the β-ferricyanide, while it gives an immediate precipitate with even very dilute solutions of the ordinary salt. Recently Bellucci and Sabatini have explained the isomer by showing that it is an isonitrile, $K_3Fe(NC)_6.H_2O$, while the ordinary salt is a nitrile, $K_3Fe(CN)_6$. In spite of all these convincing facts, Hauser and Biesalski have made an attempt to show that the β-ferricyanide is merely the ordinary salt contaminated with a trace of colloidal Prussian-blue. There is no doubt that they are absolutely mistaken about this matter. Curiously enough, although they are situated at the University of Berlin, and appear to have consulted the original articles, they have ignored entirely the bismuth reaction, without which they were not in a position to prepare the β-ferricyanide in a pure condition, since in this preparation it is very difficult to remove the ordinary ferricyanide. It appears, therefore, that they performed their experiments with mixtures of the two ferricyanides, and it is certain that their conclusions are entirely without foundation.—*Berichte*, xlv, 3516. H. L. W.

2. *Osmium Tetroxide as an Oxygen Carrier.*—It is well known that osmium through its oxides may act as a carrier for atmospheric oxygen, but this agent does not appear to have been employed for preparative purposes on account of its high cost, and probably because it has been supposed that the oxidation would proceed without a stopping point to the formation of worthless products. Upon studying this subject further, K. A. Hofmann has found that osmium tetroxide acts rather slowly as a carrier of atmospheric oxygen in cold solutions, but that the action is more rapid with oxygen at a pressure of 10 atmospheres and a temperature of 50–100° C. In this way by using 0·01 g. of OsO_4 in 200^{cc} of solution it was found that 40 per cent ethyl alcohol was oxidized chiefly to acetic acid and aldehyde in the course of 3 or 4 hours, while diluted methyl alcohol was oxidized to formaldehyde and formic acid. It was observed that the aldehydes are very slowly or not at all oxidized by this action. The very interesting discovery was made that the oxygen of chlorates is made active by the presence of osmium tetroxide,

even in neutral solutions. For instance, if a mixture of 15 g. of metallic arsenic and 10 g. of potassium chlorate is covered with 50^{cc} of water there is no reaction, even after adding 1^{cc} of dilute sulphuric acid; but if a solution of 0·015 g. of OsO_4 is added, a violent reaction takes place, with the formation of arsenic acid. The oxidation of various organic compounds was accomplished similarly with potassium or sodium chlorate, and it appears that osmium tetroxide is more efficient in such reactions than vanadic acid, or cerium salts, which have been used as oxygen carriers in some of the cases.—*Berichte*, xlv, 3329. H. L. W.

3. *A New Gasometric Method for Determining Nitric Oxide.*—The importance of nitric oxide in connection with the modern development of the utilization of atmospheric nitrogen, and the fact that there has been no exact method for determining this gas in the presence of others, have led Baudisch and Klinger to work out a new method for the purpose, which appears to be exact and simple. The process is based upon the fact that when air is brought into the presence of nitric oxide in the presence of solid potassium hydroxide potassium nitrite is produced, without the formation of any nitrogen peroxide, according to the equation

$$4NO + O_2 + 4KOH = 4KNO_2 + 2H_2O$$

The volume of nitric oxide is therefore four-fifths of the contraction. It is important that the air should be added to the nitric oxide, for when air is in excess the N_2O_3 at first formed is partly oxidized to NO_2. In order to carry out the analysis, a pipette containing a little moist potassium hydroxide in the stick form is completely exhausted of air by means of mercury, the measured gas is led into the pipette, an excess of air, also measured, is then put in, and finally the residual gas is sucked out and measured. The test-analyses given show excellent results.—*Berichte*, xlv, 3231. H. L. W.

4. *The Preparation of Organic Compounds;* by E. De Barry Barnett. 8vo, pp. 310. Philadelphia, 1912 (P. Blakiston's Son & Co.).—This American reprint of an English book is an excellent laboratory manual which includes both theoretical and practical operations. Many fundamental reactions are illustrated which are not included in other text-books. A desirable feature of the work is the selection of numerous preparations which have been taken from the patent literature. The book can be recommended for advanced students who desire an extensive training in laboratory practice. The list of references to scientific and patent literature is a very full one. T. B. J.

5. *A Dictionary of Applied Chemistry;* by Sir Edward Thorpe. Revised and enlarged edition, Vol. III. 8vo, pp. 789. London, 1912 (Longmans, Green and Co.).—The third volume of this important work of reference extends from GR to OILS. Among the large number of articles the volume contains several that deserve special mention. For example, those on the utilization of atmospheric nitrogen, on metallography, and on naphthalene (which takes up 100 pages of the book) may be noticed as particularly important and interesting. H. L. W.

6. *The Theory of Measurements;* by A. DE FOREST PALMER. Pp. xi, 248, with 16 figures. New York, 1912 (McGraw-Hill Book Co.).—This volume has been prepared primarily to meet the needs of students in engineering and advanced physics who have a working knowledge of the differential and integral calculus. It is intended not to supersede but to supplement the manuals and instruction sheets usually employed in physical laboratories. Consequently, particular instruments and methods of measurement are described only in so far as they serve to illustrate the principles under discussion.

The first seven chapters deal with the general principles that underlie all measurements, with the nature and distribution of the errors to which they are subject, and with the methods by which the most probable result is derived from a series of discordant measurements. The next five chapters are devoted to a general discussion of the precision of measurements based on the principles established in the preceding chapters. The criteria of accidental errors and suitable methods for dealing with constant and systematic errors are developed in detail. In chapter thirteen, the relation between measurement and research is pointed out and the general methods of physical research are outlined. Throughout the book, particular attention is paid to methods of computation and to the proper use of significant figures. The twenty-three tables of formulæ and numbers, which immediately precede the index, are exceptionally well selected. [In Table V, page 219, *read* $\frac{\partial}{\partial x} aU$ *for* "$\frac{\partial}{\partial x} U$."] This text should be useful to graduate students and teachers as well as to advanced undergraduate students. Everything about the volume is so complete, elegant and pertinent that both the author and the publishers deserve to be congratulated for their care and success in producing a most useful text. H. S. U.

7. *Physical Laboratory Guide;* by FREDERICK C. REEVE. Pp. x, 182, with 16 figures. New York, 1912 (American Book Co.).—This manual covers all the requirements of the "College Entrance Board" and similar Examination Boards. The guiding principle of the book may be inferred from the following quotation from the preface: " . . . the working directions in this manual are unusually full. The delusion of giving the pupil only a hint about the experiment and then expecting him to work it out for himself always results in confusion on the part of the pupil and an impossible situation for the teacher." A large number of questions, to be answered in writing by the student, are scattered through the text. Chapter X, pages 115 to 146, is entitled "Notes on the Experiments," and it amounts to a carefully prepared synopsis of the definitions and physical laws which are involved in the preceding experiments. The next chapter consists of 19 tables of mathematical and physical constants. The last chapter gives a list of apparatus required for

the experiments and also some hints for the construction of certain simple forms of apparatus, such as voltaic cells, Wheatstone's bridges, etc. H. S. U.

8. *The Energy System of Matter;* by JAMES WEIR. Pp. ix, 200, with 12 diagrams. London, 1912 (Longmans, Green and Co.).—The subject-matter of this book is divided into three parts, namely, "I General Statement," "II Principles of Inception," and "III Terrestrial Conditions." An idea of the general nature of the contents of the volume can best be gotten from the following quotations. On pages 3 and 4 we read: "Of modern research into the ultimate constitution of matter little requires to be said. It is largely founded on certain radio-active and electrical phenomena which, in themselves, contribute little information. But aided by speculative methods and the use of preconceived ethereal hypotheses, various elaborate theories have been formulated, explaining matter and its properties entirely in terms of ethereal motions. Such conceptions in their proper sphere—namely, that of metaphysics—would be no doubt of interest, but when advanced as a scientific proposition or solution they border on the ridiculous." The author, on page 194, compares the present state of physical science with its condition before the time of Copernicus, and, on page 195, he says in this connection: "Like its predecessor relating to the motion of the sun and stars round the earth, the doctrine of energy transmission between separate masses in space such as the sun and the earth cannot be sustained in the face of scientific observation. This doctrine is found on investigation to be supported not by phenomena but by the conception of an elastic ethereal medium, of whose existence there is absolutely no evidential proof, and the necessity for which disappears along with the hypothesis it supports." Taken broadly, the entire volume is devoted to showing that each heavenly body is unqualifiedly conservative in itself.
H. S. U.

9. *Electricity and Magnetism;* by SYDNEY G. STARLING. Pp. vii, 583, with 452 figures. London, 1912 (Longmans, Green and Co.).—The present volume is intended for use in senior classes, as may be inferred from the fact that a knowledge of the elements of the theory of determinants and of the differential and integral calculus is assumed. The material of the text is presented in the following order: magnetism, current electricity, electrostatics, electrolysis, thermo-electricity, electromagnetics, etc. Due attention is also given to varying and alternating currents, to electromagnetic radiation, to conduction in gases, and to radio-activity. The index is immediately preceded by 191 examples which are grouped to correspond to the preceding chapters. The text seems to be very reliable but encyclopedic, and hence it is exceptionally good for reference. On the other hand, because of the very large amount of material presented, as well as on account of the small type used throughout, the volume does not appear to be well adapted to meet the usual requirements of class-room work in this country. H. S. U.

10. *Studies in Radioactivity;* by W. H. BRAGG. Pp. x, 196, with 70 figures. London, 1912 (Macmillan and Co.).—This volume of "Macmillan's Science Monographs" deals mainly with the phenomena attending the passage of α, β, γ and X rays through matter. The researches of the author have been so bound up with the work of other investigators that, of necessity, the volume is not restricted to a systematic account of Bragg's experiments but it is limited only by the confines of the field in which the inquiries have been made. It is manifestly impossible to do justice to the argument of the text in the space at our disposal. Suffice it to say that, as is well-known, Bragg interprets the experimental evidence as showing the non-existence of *true* secondary radiation and that X and γ rays are corpuscular in nature since they are, in a certain sense, completely interchangeable with the moving electron. The investigations of the author are so important, his style is so lucid and pleasing, and the diagrams and type are so clear, that the book merits the attention of all students of radio-activity. H. S. U.

11. *Electric Lighting;* by WILLIAM SUDDARDS FRANKLIN. Pp. viii, 299, with 203 figures. New York, 1912 (The Macmillan Co.).—It seems desirable to point out the relationship existing between this book and certain earlier volumes by the same author. The present volume is intended to be a companion to "Dynamos and Motors" by Franklin and Esty. In these two volumes the physical principles underlying operating engineering rather than the principles of design have received especial emphasis. Also, the ground covered in these two books is not coextensive with the material presented in the author's "Elements of Electrical Engineering."

Some of the topics discussed in the volume to which this notice primarily refers are: installation and operation costs, electric distribution and wiring, alternating-current lines, photometry, electric lamps, lamp shades and reflectors, interior and street illumination, electrolysis and batteries, telegraph and telephone systems, and dielectric stresses. The practical value of the text is enhanced by numerous bibliographical references. The figures are clear-cut and to the point, and the manner of presentation has the same characteristics as all of the author's works, namely, lucidity and practicability. Appendix B is a list of 63 problems classified according to the respective chapters. H. S. U.

12. *Lehrbuch der Optik;* by PAUL DRUDE. Third edition, revised by E. GEHRCKE. Pp. xvi, 548. Leipzig, 1912 (S. Hirzel). —The latest edition of this standard text-book differs but little from the second (see this Journal, vol. xxiii, p. 146, 1907). Two new articles, dealing respectively with Stokes's theory of aberration and with photochemical processes in gases, have been added. The bibliographical and explanatory foot-notes have been changed to conform to the recent developments of the subject. The number of pages, however, has only been increased by ten. H. S. U.

13. *A Laboratory Manual of Alternating Currents;* by JOHN H. MORECROFT. Pp. viii, 247, 184 figures, 27 plates. New York, 1912 (Longmans, Green and Co.).—The thirty-nine experiments described are designed for the use of senior students of electrical engineering, and hence a thorough knowledge of the laws of alternating currents is assumed. In the opinion of the author most laboratory texts are conducive to mere perfunctory manipulation on the part of the student and hence he has laid special stress on the careful analysis of the test to be performed, of the different variables involved and their relations to one another, of the errors likely to be introduced, etc. Also, as far as reasonable, the student is expected to work out for himself the scheme of connections, to select the most suitable meters, and to prepare his record sheets in advance. In order that the student may thoroughly appreciate the principles involved in the construction of his measuring apparatus and that he shall know the limitations of the instruments, a more detailed analysis of the action of alternating current meters is given than may be found elsewhere. Another new feature of the text consists in a mathematical discussion of armature reaction in single and polyphase machines. The appendix includes the plates, which are reproductions of ondograph and oscillograph records. These curves have been carefully selected for the purpose of clearing up certain involved points indicated at different parts of the text. "It is the writer's opinion that much more of this type of work should be incorporated in our laboratory courses." The paper used is very good, the type and diagrams are above reproach, and no effort seems to have been spared to make the volume as useful and attractive as possible. H. S. U.

II. GEOLOGY AND NATURAL HISTORY.

1. *Cambrian Brachiopoda;* by CHARLES D. WALCOTT. Monograph 51, U. S. Geol. Surv.; parts 1 and 2, 1912, pp. 872, pls. 104.—The monograph on the Cambrian Brachiopoda by Charles D. Walcott has been going through the press for so long a time and the date of its publication so nearly coincides with the calendar year that an exact statement concerning its publication and first distribution may be of value to bibliographers. Part II (plates) was received by the U. S. Geological Survey from the Government Printing Office during the fall of 1912, the exact date being of no consequence because no copies were sent out at that time. Part I (text) was received from the Government Printing Office on December 24, 1912, and copies of both parts were sent out on December 28 to the following: Messrs. Charles Barrois, W. C. Brögger, J. M. Clarke, W. H. Dall, Karl A. Grönwall, G. F. Matthew, J. C. Moberg, A. G. Nathorst, D. P. Oehlert, J. F. Pompeckj, Charles Schuchert,

E. O. Ulrich, Stuart Weller, H. S. Williams, Carl Wiman, and the immediate distribution list of the Survey, which includes about twenty-five scientific magazines, institutions, etc, This preliminary distribution was merely for the purpose of fixing the date of publication (December 28, 1912) within the calendar year which appears on the title pages of the volumes, something which might not have happened if the entire sendings had been allowed to go forward in the usual way.

LANCASTER D. BURLING.

2. *Index to the Stratigraphy of North America;* by BAILEY WILLIS. Prof. Paper 71, U. S. Geol. Surv., 894 pages, 19 text figs.; accompanied (in separate case) by a geologic map of North America compiled by the U. S. Geological Survey in coöperation with the Geological Survey of Canada and the Instituto Geológico de México, under the supervision of Bailey Willis and G. W. Stose, 1912.—This very important publication is particularly valuable for the accompanying geologic map of North America in four sheets, making a wall map 60×77 inches. The geology on this map is shown in 42 colors, 1 of which gives the distribution of Quaternary formations, 9 Cenozoic, 8 Mesozoic, 11 Paleozoic, and 13 pre-Paleozoic. In addition there are in the text 18 sketch maps giving the areal distribution of the combined formations of a system, along with the key to references in the text where considerable of the local geology is described. This map will be of the greatest service to American geologists, and is indispensable to all teachers of geology. Its color scheme is so arranged that the major features of the continent are apparent at a distance, while the detail is readily discernible on closer view.

The *Index to the Stratigraphy of North America* is a compilation designed to explain the geologic map. The compiler, Mr. Willis, "has assembled the latest or most authoritative statements of fact and opinion, selected according to his best judgment. . . . The material selected comprises discussions of stratigraphy, some citations of fossils, and some views on correlation. The aim has been to state stratigraphic facts as fully as the data available or the scope of the work permit, and to include as much as space allows relating to faunas and correlation. Quotation is preferred, but where it was not practicable an abstract of facts has been made and the reference given."

The work was a most difficult and laborious undertaking, and the thanks of all geologists are due to Mr. Willis and Mr. Stose.

C. S.

3. *Lehrbuch der Paläozoologie. I: Wirbellose Tiere; II: Wirbeltiere;* by E. STROMER VON REICHENBACH. Pages 342 and 325, figs. 398 and 234. Leipzig and Berlin, 1909–1912.—This text-book of paleontology is now completed. It is replete with excellent illustrations, most of which are redrawn from many different sources, and the printing is of the best. The material is handled from the standpoint of classes, subclasses, and orders, all of which are briefly defined and the essential characters pointed

out and as a rule illustrated. The geologic distribution, with the more important recent literature, is the closing topic of the discussion of each class of organisms. The final chapter in the work consists of 60 pages treating of Faunal Succession, Geographic Distribution and Ecology, Paleozoology and Biogenesis, and the Vanishing of the Stocks. The book is recommended to teachers and students of paleontology. C. S.

4. *Paleolithic man.*—In sharp contrast to the dearth of fossil human remains in the Americas are the discoveries which are continually coming to light in the Old World. The latest of these is the finding near Piltdown Common, Fletching, Sussex, in gravel deposited by the river Ouse, of relics of humanity, consisting of the greater part of a brain-case and one mandibular ramus with two molar teeth. These bones were associated with water-worn eoliths, and, still more to the point, with two fragments of molar teeth of a Pliocene elephant and the water-worn cusp of a mastodon molar; in addition to the Pliocene relics were also found the teeth of hippopotamus, beaver, horse, and part of the antler of the red deer, with several unabraded early Paleolithic (Chellean) implements. Of course the youngest associated remains only serve to determine the date of the deposits and therefore seem to refer them to Lower Pleistocene time.

The skull measures 190^{mm} in length by 150^{mm} in greatest width, and the bones are nearly twice the normal thickness, the indicated brain capacity being about 1070^{cc}. Comparison with the Neanderthal type shows for the Sussex skull a much steeper forehead with only a feeble brow ridge, while the remarkably low and broad rear of the skull indicates an ape-like neck. The jaw is similar to that of a young chimpanzee but the comparatively long and narrow molars are distinctly human.

"At least one very low type of man with a high forehead was therefore in existence in western Europe long before the low-browed Neanderthal man became widely spread in this region. Dr. Smith Woodward accordingly inclines to the theory that the Neanderthal race was a degenerate offshoot of early man and probably became extinct, while surviving modern man may have arisen directly from the primitive source of which the Piltdown skull provides the first discovered evidence."—*Nature*, Dec. 19, 1912, p. 438. R. S. L.

5. *Isostasy, a rejoinder to the article by Harmon Lewis;* by John F. Hayford. Reprinted from the Journal of Geology, vol. xx, pp. 562–578, 1912.—In the Journal of Geology for October–November, 1911, Mr. Harmon Lewis claimed that Hayford had made a fundamental error in his computations on the depth and completeness of isostatic compensation,—namely, that if the assumption of complete compensation was wrong the following calculations would bring out not a true depth but such a one as would counteract the effect of the wrong assumption and thus keep the sum of the residuals small. Lewis, however, did not demonstrate his claim by actual application of his theory to Hay-

ford's data. The latter states that this could have been done with but small expenditure of time and in this article makes such an application. It is shown that for any assumed depth of compensation a degree of compensation can be calculated which will give the observed deflection of the vertical at any station. He points out, however, that on assuming a certain depth of compensation the degree of compensation is greatly different for different stations, there being overcompensation for some, undercompensation for others. This discordance of results Hayford holds to prove the error of the criticism of Lewis. The results of gravity determinations Hayford further points out to be in agreement with his computations from deflections of the vertical, the two methods of investigation thus giving mutual support.

J. B.

6. *Investigation of the Theory of Isostasy in India;* by MAJOR H. L. CROSTHWAIT, R.E., Dy. Superintendent, Survey of India. Professional Paper No. 13, Survey of India. Pp. 14, pl. I. 1912.—This paper consists of an application to India of Hayford's method of determining the depth and degree of isostatic compensation. It was assumed that compensation is uniform and complete at a depth of 113·7 km., the depth found most probable for the United States. It is shown that the residuals, the test of the accuracy of the initial assumptions, average about three times as large for India as for the United States. In conclusion Major Crosthwait states that the drawback to treating this subject by hard and fast mathematical formulæ is that we introduce into a discussion of the constitution of the earth's crust a uniform method when, in reality, probably no uniformity exists. The map of India in the back shows graphically the system in the distribution of the residuals. The narrow trough of greatly deficient density lying south of the Himalayas is a most striking feature. J. B.

7. *Effect of Topography and Isostatic Compensation upon the Intensity of Gravity* (Second Paper); by WILLIAM BOWIE. Special Publication No. 12, Coast and Geodetic Survey. Washington, D. C. Pp. 28, pls. 5. 1912.—In the previous report on the distribution of gravity over the United States 89 stations were used. In the present investigation the number has been raised to 124. The relation of gravity anomalies to the outcrops of the several geological systems is rediscussed and also the completeness of compensation. It is concluded that the average departure from complete compensation indicated by the gravity determinations is represented by a layer of rock 630 feet thick. The deflections of the vertical gave 250 feet. In neither case is the result of a high grade of accuracy but both indicate a fairly high degree of isostatic adjustment. Illustration No. 2 showing the lines of equal anomaly is especially instructive. J. B.

8. *The Making of the Earth;* by J. W. GREGORY. Pp. viii, 256; with 38 figures. New York, 1912 (Henry Holt and Co.).—This is one of the volumes of the "Home University Library of

Modern Knowledge" and is a readable volume dealing with such subjects as the nebular origin, the formation of the earth's crust, the plan of the earth, the deformation of the earth and the origin of life. It is a difficult and doubtful task to deal in a popular and yet scientific manner with subjects so speculative and on which so little is securely known. It is unfortunate that many speculative views are stated in this volume with the confidence of better demonstrated conclusions, and important difficulties if appreciated are not mentioned. Thus the lay reader will either come to regard geology as a visionary science or gain a false confidence in its more speculative aspects. J. B.

9. *The Geological Society of America.*—The twenty-fifth annual meeting of the Geological Society was held in New Haven, Connecticut, under the auspices of Yale University, from December 28 to 31. The meeting was largely attended and many interesting papers were presented. The presidential address, delivered by Prof. H. L. Fairchild on Saturday evening, was on the subject of "The Pleistocene Formations of New York State." The morning sessions for the three days were general in character, in which the entire Society united, while in the afternoon three sectional sessions were held: Group A, dynamic, structural, glacial, and physiographic, presided over by the President; Group B, stratigraphic and paleontologic, presided over by the Vice-President, Prof. David White; and Group C, petrologic, mineralogic, and economic, presided over by the Vice-President, Prof. I. C. White. A geological excursion to the neighboring trap sheets and dikes was planned for Sunday morning, but on account of bad weather had to be given up; in the afternoon the Peabody and Art Museums, and the University Library, were open for inspection.

A special feature was the evening meeting of the 29th, commemorating the centenary of the birth of James D. Dana; this was opened by President Hadley, and brief addresses followed having reference to Dana as a man, by Professor W. N. Rice; as a teacher, by Dr. E. O. Hovey; as a geologist, by Dr. G. P. Merrill; and as a zoologist, by Prof. J. M. Clarke (read by Prof. H. L. Fairchild). There was also an exhibition of the Dana books, manuscripts, diplomas, and medals in the Library.

The Paleontological Society also held its fourth annual meeting at New Haven, on December 30, 31, and the Association of American Geographers met there on December 27, 28.

10. *Gems and Precious Stones of the United States.*—Among the many interesting advance chapters of the Mineral Resources of the United States for 1911, attention should have been called earlier to that on the Gems and Precious Stones, by Dr. D. B. Sterrett. Among the points of special interest are noted the opening of an emerald mine near Shelby, N. C., yielding valuable gems; the development in the output of agate and jasper, and their related varieties of quartz; and the development of sapphire mining in Montana. It is stated that the output of dia-

monds from Cape Colony amounted to upwards of 2,000,000 carats for the year, valued at £5,400,000 sterling. The Transvaal and the Orange Free State also yielded large quantities, and some stones were obtained from the Belgian Congo. In this country, it is worth noting that prospecting in Arkansas has shown the existence of two diamond-bearing pipes, but lack of capital hindered development in 1911. The largest diamond found in the year was 8$\frac{1}{8}$ carats; another weighed 3$\frac{44}{64}$ carats.

11. *College Zoology;* by Robert W. Hegner. Pp. xxiv, 733, with 553 illustrations. New York, 1912 (The Macmillan Company).—This book is designed especially for students in American colleges who require a general survey of the whole animal kingdom in a single course of study. The type system is followed, by selecting in each group the representative which is the most familiar or of the most economic importance. More attention is devoted to the functions of the organ systems of the various groups than to strictly anatomical details. An introduction of 25 pages is followed by 375 pages of descriptions of invertebrate animals (of which ten phyla are recognized) and about 300 pages of vertebrates. This seems a reasonable distribution of the available space, for each group is adequately treated. The illustrations are chosen mainly from well-known works, and are quite satisfactory. The book is remarkably free from errors and unessential details, and is eminently suitable for courses in general or economic zoology. W. R. C.

12. *House-flies, and how they Spread Disease;* by C. G. Hewitt. Pp. xii, 122. Cambridge, 1912 (The University Press). New York (G, P. Putnam's Sons).—This little volume of the Cambridge Manuals of Science and Literature contains an exceptionally interesting account of the structure, habits, life history, and economic importance of this common household pest. Medical men and others are now beginning to realize the responsibility of this agent in the transmission of some of the most dreaded of human diseases. The general knowledge of the simple facts so clearly presented and a wide application of the common sense remedies proposed would materially increase the health and happiness of the human race. W. R. C.

III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *Journal of the Academy of Natural Sciences of Philadelphia. Second Series, Volume XV. Published in Commemoration of the One Hundredth Anniversary of the Founding of the Academy*, March 21, 1912. Pp. cxlii, 614; with 49 plates. Philadelphia, 1912 (published by the Academy).—An occasion so rare and notable in the history of American science as the centenary of the founding of the Academy at Philadelphia well deserves to be commemorated by the handsome and massive volume recently issued. The sessions of the Academy, extending from March 19 to 21, 1912, were attended by a large body of

scientists, including many delegates from universities, academies and scientific societies distributed all over the world. Pages lii–cxxxiii of this report are devoted to an interesting series of selected letters for the most part brought by individuals representing the institutions invited to attend. In addition, there is given a brief summary of the proceedings, and the addresses of the Mayor, the Hon. Rudolph Blankenburg, and of the President, Hon. Samuel G. Dixon, are given in full. It is well known that the remarkable development of the Academy in recent years, and the vigor with which it begins its second century, are largely due to the efforts of Mr. Dixon.

Part II contains a series of twenty-two original memoirs illustrated by a large number of plates of admirable execution. It is impossible to reproduce here the list of papers, but it is interesting to note that the one first in order is by the late Dr. Thomas H. Montgomery, Jr., of the University of Pennsylvania, whose early death on March 19, 1912, robbed biology of one of its most prominent students. It should be added that the present volume has been carried through by Dr. Edward J. Nolan, as editor.

2. *Report of the Secretary of the Smithsonian Institution*, Dr. Charles D. Walcott, *for the year ending June 30, 1912.*—Pp. iii, 110, with two plates. Washington, 1912.—The Secretary, in referring to the trust fund recently founded in connection with the Smithsonian by Mrs. E. H. Harriman for carrying on certain research work, expresses his desire to establish a number of research associateships on a similar basis, allowing able men to carry forward research work without the usual limitations. Something of this kind has already been accomplished for a number of years by the Hodgkins fund. In connection with a gift of a valuable set of patents by Dr. Frederick G. Cottrell, of the U. S. Bureau of Mines, it is stated that a Research Corporation has been established under the laws of New York to acquire and make available inventions and patents, using them also as a source of income ; further, to apply all profits thus derived for the advancement of scientific investigations through the agency of the Smithsonian. It is noted that the completion of the new National Museum has progressed so rapidly that with the beginning of the fiscal year 1913, the building will be entirely equipped and all the exhibition halls opened to the public. During the past year the Museum has been open on Sundays, and on the first day, October 8, 1911, nearly 15,500 visitors were present. The Rainey and the Frick African expeditions have yielded important results and added largely to the collections. Mention is also made of various other expeditions and special works, among which are to be particularly noted those in ethnology and further the studies in Cambrian paleontology by Dr. Walcott during the spring and summer of 1912 in British Columbia. Among other points of interest in this report is the mention of the bill now pending in Congress to erect, on Armory Square, a George Washington memorial building at a cost of not less than $2,000,-

000, in which large conventions can be held, and which would also be the headquarters of scientific, patriotic, and other organizations. It is proposed to have an endowment fund of not less than $500,000 to be administered by the Smithsonian regents.

With reference to the work of the Astrophysical Observatory under the charge of Dr. C. G. Abbot, the following summary is given: "The year has been notable for expeditions to Algeria and California to test the supposed variability of the sun by making simultaneously at these two widely separated stations spectrobolometric determinations of the solar constant of radiation. The measurements in Algeria agree with earlier ones at Washington and Mount Whitney and indicate that Mount Wilson values are systematically a little low. Apart from this systematic error the accidental differences between Algerian and Mount Wilson determinations were only 1·2 per cent, indicating an average accidental error of a single solar constant determination at one station of only 0·9 per cent. So far as yet reduced, *high solar constant values obtained in Algeria coincide with high values at Mount Wilson and vice versa.* A solar variation of 4 per cent was indicated at both stations in the first half of September, 1911. Many values remain to be computed, but it can now hardly be doubted that the outcome will prove conclusively the irregular short-period variability of the sun."

3. *Annual Report of the Board of Regents of the Smithsonian Institution, showing the Operations, Expenditures, and Condition of the Institution for the year ending June 30, 1911.* Pp. xii, 688, with numerous illustrations. Washington, 1912.—This volume contains the report of the Secretary already noticed (see vol. xxxiii, p. 165) similar to the later report above noticed. In addition, the general Appendix, pp. 109–688, contains the usual series of scientific papers and memoirs, admirably selected to present to the intelligent public a summary of progress made during the year in the many branches of science. This plan has been followed out with excellent results for a considerable period of years.

4. *Report of the Librarian of Congress*, HERBERT PUTNAM, *for the fiscal year ending June 30, 1912.* Pp. 235, with 6 illustrations. Washington, 1912.—It is interesting to note that although the Library of Congress is supported by the Government, and was originally planned particularly for the benefit of its officers, it has yet grown to have a first place among the great libraries of the country, and is receiving from time to time notable gifts from private individuals. The present volume records the presentation, by Mr. Jacob H. Schiff, of a collection of Hebraica comprising nearly 10,000 volumes and pamphlets, and covering the period from the beginning of Jewish national life to the present date. It was brought together by Mr. Ephraim Deinard of Arlington, New Jersey. Another important addition is the library of Dr. Henry Carrington Bolton, embracing 1631 volumes and pamphlets, and particularly rich in the bibliography

of chemistry. It is presented by Dr. Bolton's widow, Mrs. Henrietta Irving Bolton. A considerable number of other gifts are noted, among which may be mentioned the Karow collection of Napoleona gathered by the late Major E. W. Karow of Savannah and presented by his widow. It includes 300 volumes, many of them in fine bindings. A notable gift of books, pamphlets, and periodicals, relating to Mexico and Central America, has been presented by the Mexican embassy. The Librarian's report also contains many other facts of interest, particularly to those engaged in similar work.

5. *Bjerknes' Dynamic Meteorology.*—"A prophet is never without honor save in his own country," and possibly this is the reason why the great work on "Dynamic Meteorology" by Victor Bjerknes and his several colaborers had to be published first in America, and at the expense of the abundant funds of the Carnegie Institution of Washington, before it could be accepted in Germany and reprinted by F. Vieweg & Son of Brunswick. It undoubtedly was Bjerkes' hope that American students would be the first to awake to the importance and elegance of his graphic methods, but it seems that the "International Commission on Scientific Ballooning" have already adopted his ideas and have created the demand to which Vieweg is now ministering. In a circular issued by Vieweg we are informed that the German edition will comprise four volumes, of which the first volume with charts is already published, relating to statics. The second volume, relating to kinematics, is in press, while the dynamics and the thermodynamics will be published later. The price of the first German volume, with charts, 36 marks, is slightly in excess of the price advertised by the Carnegie Institution, viz., $5.00, but that is doubtless owing to the expense of the atlas of charts.

The early publications of Bjerknes were translated and published in the Monthly Weather Review for 1900, special memoirs by Sandstrom were translated and published in the proceedings of the American Philosophical Society, 1905, vol. xxi, and in the Bulletin of the Mount Weather Observatory, 1910 and 1912, so that the works of these distinguished Norwegians have long been familiar to Americans. Bjerknes' object is to make rational methods of mechanics and physics practically useful in the study of the atmosphere and the ocean. Hitherto meteorology and hydrography have been empirical sciences in which as yet only very limited use has been made of methods used in mechanics and physics. It is not to be doubted that the great movements of the atmosphere of the ocean are accomplished in accordance with the laws of mechanics; all phenomena that occur in the atmosphere and ocean connected with these motions are also due to known laws of physics, especially thermodynamics; therefore we are justified in assuming that a great advance will be realized in the study of the air and the ocean as soon as methods are found to practically apply in these branches of science the knowledge that is already well established in mechanics and physics. The

Bjerknes "Dynamic Meteorology" will be both a handbook for the working meteorologist and hydrographer and also a treatise for the students to these sciences: it is also the most important of all applications of Vector Analysis. C. A.

6. *Founders of Modern Psychology;* by G. STANLEY HALL. Pp. vii, 471, with 6 portraits. New York and London, 1912 (D. Appleton and Company).—The basis of this volume is to be found in six lectures given by the author a year since at Columbia University. They are rather popular than technical in character, but give a most interesting account of six men whose original work has contributed largely to the development of modern psychology in its varied lines. The author himself came under the direct influence of four of these men when a student in Germany from 1870–73; hence he writes of them as only one who has had direct personal acquaintance can do. The six philosophers discussed in this volume are characterized as follows: "Edward D. Zeller, the historian of ancient philosophy; Edward von Hartmann, the philosopher of temperament; Herman Lotze, the harmonizer; Theodore Fechner, the animist; Herman von Helmholtz, the ideal man of science; and Wilhelm Wundt, a scientific philosopher."

7. *Publications of the Princeton University Observatory.*—The following has recently appeared: Contributions, No. 2. Photometric Researches: The Algol-System Z Draconis; by R. S. DUGAN. Pp. 44. Princeton, 1912.

8. *Publications of the Allegheny Observatory of the University of Pittsburgh.*—Recent issues are as follows: Volume II, No. 17. Tables for the true anomaly in Elliptic Orbits; by FRANK SCHLESINGER and STELLA UDICK. Pp. 155–190.

No. 18.—The Orbit of B. D. +43° 92; by STELLA UDICK. Pp. 191–196.

9. *Libya Italica. Terreni ed Acque, Vita e Colture della Nuova Colonia;* by P. VINASSA DE REGNY. Pp. xv, 214; plates xxxiv. Milano, 1913 (Ulrico Hoepli).—Recent events by which a large tract in North Africa has passed under Italian rule give a special interest to this work by the author, who is a professor in the University of Parma. It is based largely upon original observations made in traveling through the region sometime since, and covers the various points of interest connected with this region; that is, its physiography; vegetation, both native and cultivated; the life, and other points. There is a chapter on the geology, with a colored geological map, and a series of thirty-four photogravure plates put vividly before the reader the scenery and many other points of interest connected with this part of northern Africa.

10. *Archiv für Zellforschung:* Editor, Dr. RICHARD GOLDSCHMIDT, Professor in the University of Munich. Leipzig (Wilhelm Engelmann).—This well-known journal, devoted to original investigations of cytological phenomena, has recently completed its eighth volume. The last three numbers of this volume include

the following papers:—A. Russo: Aumento dei granuli protoplasmatici nell' oocite delle Coniglie iniettate con Lecitina, loro diminuzione nelle Coniglie digiunanti e loro natura lipoide e mitocondriale; G. Kautzsch: Studien über Entwicklungsanomalien bei Ascaris; G. Arnold: The rôle of the chondriosomes in the cells of the guinea pig's pancreas; O. Koehler: Über die Abhängigkeit der Kernplasmarelation von der Temperatur und vom Reifezustand der Eier; H. Kupelwieser: Weitere Untersuchungen über Entwicklungserregung durch stammfremde Spermien; J. Schmalz: Zur Kenntnis der Spermatogenese der Ostracoden; H. Erhard: Studien über Nervenzellen; H. Hoven: Contribution à l'étude du fonctionnement des cellules glandulaires; A. Pensa: Osservazioni di morfologia e biologia cellulare nei vegetali; J. P. Munson: A comparative study of the structure and origin of the yolk nucleus. L. L. W.

OBITUARY.

Dr. LEWIS SWIFT, the astronomer, died on January 5 at Marathon, N. Y., at the age of nearly ninety-three years. Born in 1820, at Clarkson, N. Y., he early went into business but later became interested in astronomy and by his great industry and acute powers of observation he discovered a remarkable number of comets and nebulæ. His work brought him honor and reward in medals from many scientific bodies at home and abroad. He was made Director of the Warner Observatory at Rochester in 1882, and later of the Lowe Observatory on Echo Mountain, California.

Dr. GEORGE A. KOENIG, Professor of Chemistry in the Michigan School of Mines, died in Philadelphia on January 14 at the age of sixty-eight years. He was much interested in mineralogy and contributed many papers on mineralogical subjects including the description of several new species.

Dr. ERNST VON KOKEN, Professor of Mineralogy and Geology in the University of Tübingen, died after a long illness on November 24 at the age of fifty-two years. In his death geology, and more especially paleontology, has lost one of its best students and teachers. Since 1899 he had been one of the three editors of the Neues Jahrbuch für Mineralogie und Paläontologie, and was an honorary member of the Paleontological Society in this country. He is best known to Americans through his works: "Die Vorwelt und ihre Entwicklungsgeschichte," 1893; "Die Leitfossilien," 1896, and "Indisches Perm und die permische Eiszeit," 1907.

Mr. S. A. SAUNDERS, the English astronomer, noted for his work on the moon, died on December 8 at the age of sixty years.

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SCIENTIFIC INTELLIGENCE.

Established by **BENJAMIN SILLIMAN** in 1818.

THE AMERICAN JOURNAL OF SCIENCE.

EDITOR: EDWARD S. DANA.

FOURTH SERIES

VOL. XXXV—[WHOLE NUMBER, CLXXXV].

No. 207—MARCH, 1913.

NEW HAVEN, CONNECTICUT.
1913.

THE TUTTLE, MOREHOUSE & TAYLOR CO., PRINTERS, 123 TEMPLE STREET.

Published monthly. Six dollars per year, in advance. $6.40 to countries in the Postal Union; $6.25 to Canada. Remittances should be made either by money orders, registered letters, or bank checks (preferably on New York banks).

THE

AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

Art. XIX.—*On the Effect of High Pressures on the Physical and Chemical Behavior of Solids;* by John Johnston and L. H. Adams.

Contents.

Am. Jour. Sci.—Fourth Series, Vol. XXXV, No. 207.—March, 1913.

INTRODUCTORY.

ANYONE who has occasion to study the literature pertaining to the effect of high pressures on solid substances will be struck by the mass of contradictory statements to be found there; in the present paper an endeavor is made to reconcile some of these contradictions, to define—as impartially as may be—the present state of our knowledge of the subject, and to indicate the conclusions which may justifiably be drawn from the evidence at hand. Much of the existing confusion would appear to be due to a neglect to observe the distinction between the effects of uniform pressure and of compression which does not satisfy that condition; in other words, it is due to a misinterpretation of the results obtained. In other cases,—as, for instance, in determining the effect of pressure in promoting chemical reaction between solids—indefensible criteria have been employed to ascertain the magnitude of the change produced.

The question of the effect of high pressures on the behavior of solids has been the subject of numerous isolated papers, but has not been very systematically investigated hitherto, except perhaps by Spring. Unfortunately for the conclusive character of Spring's work, some aspects of it have been seriously called in question, while other parts have been, according to Spring's own statement,* misinterpreted or misunderstood. Now Spring's work has been quoted—and very often not at first hand—by the writers of a very large number of chemical and geological text-books, monographs and papers, who apparently were unaware of the fact that many of Spring's statements had been challenged and even disproved; so that these errors and misinterpretations seem in a fair way to be perpetuated.

Accordingly, in view of its great importance, for the science of geology in particular, it seemed desirable not only to review this subject but to attempt a critical discussion of it. This discussion is based on the work recorded in the literature;† though with regard to a few of the doubtful points, experiments were undertaken with the object of reaching a decisive conclusion.

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* Bull. Acad. Roy. Belg. (3), xiv, 595–8, 1887; this Journal (3), xxxvi, 286–9, 1888.

† To avoid possible misunderstanding, the authors desire to state here specifically that they have endeavored to refer to all papers which appeared to contain anything material to the discussion in hand and to apportion to each author the credit to which he is entitled for having made some positive advance or corrected some previous error. Further, it may be as well to state that it is no part of the plan of the present paper to discuss completely the effect of pressure on systems containing a liquid or vapor phase, e. g. solutions and their properties (electrical conductivity, etc.); and, therefore, work along these lines is referred to only incidentally.

In the discussion of the effects of pressure on solids,* it is of the utmost importance to notice that the effects of compression depend upon its mode of action; they are different, namely, according as we are dealing with pressure uniform in all directions (true hydrostatic pressure or cubic static pressure) or with a mode of compression which does not satisfy this condition;† in other words, the effects vary—as indeed is almost obvious—according as the solid retains its form unchanged or undergoes deformation.

It is also essential to note that thermodynamic reasoning is applicable only to those processes which are, ideally at least, reversible, but not to irreversible processes or changes of state.‡ Moreover, we must recognize that even with reversible processes we can draw useful conclusions only when the conditions are such that the rate at which equilibrium can be established is appreciable, or in other words, only when we are dealing with cases of true, as distinguished from apparent or false, equilibrium.

The importance of these distinctions has not been properly appreciated by many writers. In fact, this neglect is responsible for most of the existing confusion concerning the effect of high pressures and the significance of this effect in geological phenomena. In view of this confusion it has seemed to the writers necessary to discuss at some length the differences between the effects of uniform and of non-uniform pressures and to go somewhat fully into the experimental work on which some of the assertions in the literature have been based, if we are to have a clear notion of the nature and range of the conclusions which may properly be drawn from this work.

THE GENERAL EFFECTS OF UNIFORM PRESSURE.

The effects produced by pressure which is uniform in all directions are in general completely and easily reversible; the original state of the system being regained when the pressure is removed. Consequently the magnitude and direction of

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* The term *solid* we use throughout this paper to denote a *crystalline aggregate.*

† A non-uniform compression can always be resolved into a uniform pressure and a shearing stress, the latter being the effective factor in producing deformation or distortion.

‡ A change of state, or the process by which it is effected, is called *reversible* when the system can be restored to its original condition without giving rise to any residual effect in the surroundings. A change in state, or a process, is irreversible when this is not the case (e. g. the production of heat by mechanical friction or by electrical resistance). After an irreversible change has taken place, it is in general possible to restore the *system* to its original condition, but only by doing upon it a larger quantity of work than was obtained from it, so that the original condition of the *surroundings* is not reproduced.

these changes can be predicted from thermodynamical considerations. For instance, the change of melting point produced by uniform pressure can be calculated if we know the heat change and volume change accompanying the process of melting. The differential equation connecting the change of melting point (dT) with change of pressure (dP) is

$$\frac{dT}{dP}=\frac{TdV}{\Delta H} \tag{I}$$

where T is the absolute temperature of melting, dV the volume change and ΔH the heat change which accompany melting of the substance at T. In order to integrate this equation rigorously, it is necessary to know how dV and ΔH vary with pressure and temperature. The exact magnitude of these variations is not known in general; but, fortunately, their effect is slight and may for most practical purposes be neglected. Consequently we may use the following form of the equation to calculate the change of melting point (ΔT_2) produced by a change of pressure (ΔP_2, expressed in atmospheres*):

$$\frac{\Delta T_2}{\Delta P_2}=\frac{T(V_l-V_s)}{41{\cdot}30\,Q} \tag{II}$$

wherein Q is the heat of melting in calories per gram, and V_l and V_s the respective volumes of one gram of substance at the melting point in the liquid and the solid state. An example of the agreement between calculation from this formula and actual observation of the effect of pressure on the melting points of tin, bismuth, cadmium and lead is afforded by the following table, taken from a former paper from this laboratory;† the divergences are such as are to be expected in view of the present uncertainty in the values of Q, the latent heat of melting:

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* That is, true atmospheres (1033 g. per sq. cm.).

† Johnston and Adams, this Journal, xxxi, 516, 1911; Zs. anorg. Chem., lxxii, 29, 1911. It should be observed that, through inadvertence, the numerical factor (42720) made use of in the paper here cited is wrong: it is appropriate to pressures reckoned in grams per sq. cm. Substitution of the correct factor (41·30 for one atmosphere, as given above) leads to calculated values 3 per cent higher than those given in column IV of the table of the previous paper; but this makes no essential difference to anything there stated, for it is reasonably certain that the values of Q there used are not at present known with an accuracy of 3 per cent. For instance, the values recorded in Landolt-Börnstein-Meyerhoffer Tabellen show divergences in some cases of 10 per cent and it is hardly possible to determine which of these are most reliable.

Table I.—Effect of Uniform Pressure on the Melting Points of Certain Metals.

Metal	Latent heat cal. per gram Q	Vol. change on melting $V_l - V_s$	ΔT per 1000 atm. calc. from equation II	ΔT per 1000 atm. observed	Probable error[1] of coefficient in previous column
Sn	14·25	0·003894	+3·45	+3·28	±0·02
Cd	13·7	0·00564	+6·10	+6·29	±0·04
Pb	5·37	0·003076	+8·59	+8·03	±0·03
Bi	12·6	−0·00342	−3·67	−3·55	±0·08

[1] For calculation of the probable error of the coefficient, see Merriman, Method of Least Squares, 6th ed., Chapter on the Precision of Observations.

The melting point of nearly all substances is raised by uniform pressure. For metals (and in all probability for most substances) this change of melting point is not very large—in the neighborhood of 10° (or less) per 1000 atm.;* but for many oils and organic substances (wax, naphthaline, etc.) the change may amount to 30° or 40° per 1000 atmospheres. Consequently, with substances of the latter class whose melting point is close to the ordinary temperature, we should be justified in stating that uniform pressure increases their rigidity.

In passing it may be observed that by reason of this comparatively large effect most ordinary oils become solid at high pressures; consequently pressure transmitted by an oil may cease to be uniform in character at high pressures. For instance, Kahlbaum Roth and Siedler,† using castor oil, found that their metal cylinders had been slightly deformed at the highest pressures (above 10,000 atmospheres), though they failed to attribute this to the real cause—a lack of uniformity consequent upon solidification of the oil. Even liquids ordinarily so light and mobile as kerosene or gasolene become thick and viscous at high pressures, the former around 8,000 atmospheres, the latter around 20,000 atmospheres.‡

Uniform pressure may promote chemical reaction between solids under specified conditions characteristic of the particular reaction, but in general it will not do so,§ except in so far as it has an effect on the rate of reaction, which effect is probably

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* It is understood here that the pressure is acting on both solid and liquid phases. If it acted on the solid phase alone, the effect would be many times as great (compare p. 214).

† Zs. anorg. Chem., xxix, 258 et seq., 1902.

‡ Bridgman, Proc. Am. Acad., xlvii, 337, 1911.

§ This statement would require some modification for systems containing an appreciable amount of a liquid or vapor phase.

small. In general, therefore, the influence of uniform pressure upon reactions between solids is likely to be very slight.

THE GENERAL EFFECTS OF NON-UNIFORM COMPRESSION.

The effects produced by exposure to non-uniform compression are in general permanent; that is, the original state of the system is not re-established when the compression ceases. The effect of differential compression may be resolved into two parts: that due to a (smaller) uniform pressure and that due to a shearing stress,* the latter being the preponderating effect. The mere fact that "flow," or deformation, of the compressed material occurred is sufficient evidence that unequal stresses were set up; in other terms, that the compression was not uniform.

In most of the work recorded in the literature the solid substances were subjected to non-uniform compression, as is evident from the author's description of his apparatus and method of working. The discussion of this work (*postea*, p. 223), therefore, brings out in a more detailed way the effects produced on subjecting solid substances to compression of this type. Before proceeding to this, however, we shall consider whether we can adopt any plausible theoretical attitude which will harmonize the various observations of the effect of non-uniform pressure.

Such a standpoint can be attained if we assume that every *permanent* deformation of a crystalline aggregate is conditioned by, and consequent upon, a *real* melting;† the whole of the solid aggregate does not of course melt, but only those portions (particles) of it which at any instant bear the brunt of the load. This assumption, which in an indefinite form has frequently and more or less unconsciously been made use of,‡ is not so violent as at first sight it might seem to be; as we hope to show in what follows.

Granting for the moment that the above assumption is correct, it follows that the forces which produce deformation are competent to cause the melting point to be lowered to about the ordinary temperature; otherwise we must suppose that the heat developed during the friction accompanying deformation is sufficient to raise the temperature of some of the particles to their ordinary melting-point—a supposition which is less probable, for Spring found that he could in his apparatus subject

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* In precisely the same way a tensile stress can be resolved into a dilatation and a shearing stress.

† Evidence in support of the plausibility of this assumption is adduced later (p. 219).

‡ For instance, it is common knowledge that there is a general parallelism between the mechanical properties of the metals and their melting points, those with the higher melting points being the stronger, and *vice versa*.

gunpowder to high compression without causing it to explode. Now uniform pressure acting equally upon both the solid phase and the liquid phase (produced on fusion) causes a lowering of melting-point only in a very few exceptional cases* and hence its action is incompetent to account for the facts.

It can be shown, however, that if the pressure (P) acts on the solid phase but not, or not to the same extent, on the liquid phase, the melting-point of the solid is always lowered, and by an amount which is many times as great as when the same pressure (P) acts on both phases simultaneously.† For pressure of this type, we shall, for convenience in what follows, use the term "unequal" pressure. Such unequal pressure may be pictured as occurring when an aggregate of fine crystals is compressed, the liquid formed by the melting flowing into the interstitial spaces, and in this way being subject to a smaller pressure than the adjacent solid particles.‡ Moreover, if the possibility of a partial melting under stress be admitted, the force can be imagined only as acting on the solid to a much greater extent than on the liquid phase.

In formulating the assumption made use of throughout this paper, we have stated "that every *permanent* deformation of a crystalline aggregate is conditioned by, and consequent upon, a real melting," using the word aggregate advisedly. Firstly, because the experimental work which we are here considering deals exclusively with systems made up of a large number of crystals not regularly oriented; secondly, because systems composed of a single crystal, or possibly also of a number of similar crystals similarly oriented, exhibit phenomena which can be accounted for without assuming that a partial melting has taken place. The phenomena especially referred to are those connected with the presence in crystals of what are termed cleavage and gliding planes; such properties appear to be somewhat analogous to the quality of brittleness in metals, though of course metals, being agglomerates, do not show a perfectly regular fracture. The above analogy holds moreover in this, that, while the viewpoint adopted in this paper serves to correlate all those properties of metals for which quantitative measurements have been made, it does not aid us in

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* Water (though only with pressures less than about 2300 atm.) and bismuth are the best known examples.

† Cf. Ostwald, "Lehrbuch der Allgemeinen Chemie," 2 Aufl., ii, II, 374–9; Roozeboom, "Heterogene Gleichgewichte," i, 213–7. (The main part of both of these is quoted by Doelter, Physik. Chem. Mineralogie, Leipzig, 1905, pp. 160-2). Cf. also equation IV, p. 214, postea.

‡ It will of course in general freeze again immediately; (cf. postea, p. 215, where other examples are given) but failure to do so is not necessarily prejudicial to the success of the hypothesis—so long, at least, as the amount melted is a very small fraction of the whole, a condition which in practice would seem to be always satisfied (see also p. 250).

establishing a parallelism between the brittleness of a metal and any other of its properties, just as it appears to be valueless when applied to the case of cleavage or of gliding planes in crystals. The discussion of these phenomena formed no part of the plan of the present paper; we wish, however, to state explicitly our conviction that the occurrence of cleavage and of gliding planes, which renders possible some degree of permanent distortion of a crystal, is a phenomenon which may well be totally different in character from the permanent deformation of a crystalline aggregate; further, that the views which we advocate with reference to the latter case and the conceptions which petrologists make use of to account for the former case,* are by no means mutually exclusive, and may indeed supplement one another.

Calculation of the Effect of Unequal Pressure Upon the Melting Point of Crystalline Substances.

In order to determine the magnitude of the effect of unequal pressure upon the melting point of crystalline substances we must make use of thermodynamical reasoning, which is, as we have noted above, applicable only to those processes which may be classed as reversible.† Now it might at first sight appear that this particular process does not satisfy the conditions for reversibility; for, according to our hypothesis, it results in a practically irreversible permanent deformation of the body as a whole. But this total deformation we regard as the aggregate effect of a large number of what might be termed individual meltings, and there is no more reason to doubt the thermodynamic reversibility of these individual meltings than there is to question the validity of applying thermodynamics to the case of melting under uniform pressure. Tammann‡ indeed has stated that he doubts the thermodynamic admissibility of the derivation of the formula for the lowering of equilibrium temperature by unequal pressure, but this view of the matter is not shared by all of those who have considered the question; for instance, it is not shared by Roozeboom,§ Ostwald,‖ LeChatelier,¶ or by Nernst,** who writes "Die thermodynamishe Behandlung auch dieses Falles ist exakt durchzuführen."

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* It may be noted that these conceptions are of little help in accounting for, or correlating, the experimental observations discussed in the body of the present paper.

† See footnote p. 207.

‡ Ann. Phys. (4), vii, 198, 1902; Krystallisieren und Schmelzen (Leipzig, 1903), pp. 173–81.

§ Heterogene Gleichgewichte, i, 213.

‖ Lehrbuch der Allgemeinen Chemie, 2 Aufl., ii, II, 374–379.

¶ Zs. phys. Chem., ix, 338, 1902.

** Theoretische Chemie, 5 Aufl., p. 663.

Derivation of the Formula.—The derivation of the formula by means of which the effect of unequal pressure on a substance is computed is based on the thermodynamical fact that pressure acting on any phase increases the "activity" of that phase, or its tendency to pass over into another phase; in other terms, pressure acting only on the solid phase increases its vapor pressure and hence increases its solubility (in any particular solvent) and lowers its melting point. Into the steps in the derivation of this formula it is unnecessary to enter here;[*] the final differential equation is:

$$\frac{dT}{dP} = \frac{TV_s}{\Delta H} \qquad \text{(III)}$$

which expresses the lowering of melting point by unequal pressure in terms of the absolute melting point (T), the molecular volume (V_s) of the solid at the temperature and pressure in question, and (ΔH) the molal heat of fusion unde those conditions. The quantities V_s and T are always positive, but ΔH (as here used) is always negative; hence application of excess pressure on the solid phase *always* lowers the melting point.[†]

If we compare the melting point depressions (dT_1 and dT_2 respectively) produced by the same excess pressure (dP) acting on (1) the solid phase alone, (2) both phases; that is, if we combine equations III and I, we obtain the result[‡]

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[*] It is discussed in another paper: see J. Am. Chem. Soc., xxxiv, 788–802, 1912; Zs. anorg. Chem., lxvi, 361–79, 1912.

[†] This lowering is, of course, relative to the melting point when that pressure which now acts on the liquid alone (the solid being subject to pressure in excess of this) acts on both solid and liquid. In other terms: if the melting point is denoted by T with subscripts and superscripts to represent the pressure acting on the solid phase and liquid phase respectively, then $T^{P}_{P+\Delta P}$ is always lower than T^{P}_{P}, the magnitude of this lowering being dependent on the excess of pressure ΔP acting on the solid. Now T^{P}_{P} may be higher, or lower, than $T_1{}^1$ (the ordinary melting point at atmospheric pressure), according as the volume change on melting is positive or negative; consequently, in some cases, $T^{P}_{P+\Delta P}$ may be higher than $T_1{}^1$, but this will be only when ΔP is small compared to P, a contingency which, we believe, does not affect the main considerations advanced in this paper. Similar considerations apply, *mutatis mutandis*, to the increase in solubility caused by unequal pressure.

[‡] For a proof of this equation (in slightly different form) by other methods see J. H. Poynting, Phil. Mag. (5), xii, 32, 1881; G. N. Lewis, Proc. Amer. Acad., xxxvi, 145, 1900; xliii, 268, 1907; or Zs. phys. Chem., xxxv, 346, 1900; lxi, 139, 1908. The result is stated by LeChatelier (Zs. phys. Chem., ix, 335, 1892), who applies it to several problems of geological interest: cf. the paragraphs which follow.

$$\frac{dT_1}{dT_2} = \frac{V_s}{dV} = \frac{V}{V_s \quad V_l} \qquad \text{(IV)}$$

or expressed in words, the ratio of the lowering of freezing point of the solid phase, when this alone is subject to a given pressure, to that observed with the same (given) pressure acting uniformly on both phases, is equal to the ratio of the (specific) volume of the solid phase to the change of (specific) volume on freezing.

This equation shows how many times greater the melting point lowering is when the pressure acts only on the solid phase. For example, the melting point of ice is lowered by unequal pressure 12 times as much (or 0·09° per atm.) as by uniform pressure (0·0075° per atm.); in general $\Delta T_1/\Delta T_2$ is much greater than 12, because the fractional change of volume accompanying melting is usually much smaller than it is in the exceptional case of ice.

In a paper first published in 1894, E. Riecke* discussed the effect of a one-sided pressure (stress) on the melting point of ice; quite recently he has re-stated his conclusions in a second paper†, the general reasoning of which—apart from the mathematical formulæ—is identical with that of the paragraphs, immediately subsequent to this, dealing with regelation and with the influence of unequal pressure upon solubility. Riecke's formula for the lowering of melting point of ice effected by the stress Z (tensile or compressive) is

$$\Delta T_1 = -aZ^2$$

where (for ice) a has the value 0·00036 when Z is expressed in kg. per sq. cm.‡; but he appears to consider the formula valid only for small values of Z. For this reason, and for the reason that Riecke's formula was developed, and therefore is valid only for the case of a single crystal, his formula is less generally applicable than equation III (p. 213) of the present paper; moreover, within its range, it leads to much smaller values of the lowering of melting point.§

The divergence between the numerical results of the two formulæ is, so far at least as the arguments of the present paper are concerned, of secondary importance, for in general we are altogether ignorant of the nature and magnitude of the stresses to which rocks have been exposed. The important thing, especially from a geological standpoint, is the princi-

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* Nachr. Ges. Wiss. Göttingen, 1894, 278; Ann. Physik, liv, 731, 1895.

† Centralblatt Min. Geol., 1912, 97–103, q.v.

‡ One atmosphere = 1·033 kg. per sq. cm.

§ With ice, the lowerings produced by 1 and 10 atmospheres are 0·00037° and 0·037°, according to Riecke; 0·09° and 0·9°, according to equation III.

ple,—namely, that non-uniform pressure does cause a lowering of melting point,—which follows either from Riecke's formula or from the equations of the present paper. Equation III can, however, be applied much more generally, for it holds for crystalline aggregates and is not subject to any limitations as regards the magnitude of the effective stress. Hence the general principle has a much wider significance in the co-ordination of geological observations than has hitherto been attributed to it.

The Phenomenon of Regelation.

This type of compression accounts easily for regelation, a phenomenon which cannot in general be produced by uniform pressure, because uniform pressure raises the melting point of most substances.

Consider a block of ice at 0° supporting a loaded wire. The pressure exerted by the wire depresses the melting point of the ice by the amount Δt; immediately beneath the wire, therefore, we have at any instant a thin layer of ice at $-\Delta t$ in equilibrium with water at $-\Delta t$. The water escapes round the wire and so comes in contact with ice at 0°; such a system is, however, unstable, for under these conditions water cannot remain subcooled. Consequently the water freezes, thus forming again a solid block above the wire.

The process by which a mass of loose snow is compacted into a block of ice is identical with this. The pressure, due to the superincumbent material, lowers the melting point at the surface of contact of adjacent grains; the water at $-\Delta t$ flows into the interstices where the pressure is smaller and freezes again. This process continues until the interstices are all filled up, that is, until a solid block of ice is formed.

According to Le Chatelier*: "This is a type of consolidation which is in every respect comparable with that which I have given for the setting of cement. In either case we have a solid substance, which is not in equilibrium—either because of its chemical condition or because it is compressed—in contact with a supersaturated solution or vapor, the temporary formation of which renders possible the return to equilibrium conditions."

Influence of Unequal Pressure upon the Solubility of Solid Substances.

Considerations in every respect analogous are applicable to systems of a solid in contact with water or other solvent: in such cases pressure acting in excess on the solid increases its

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* Zs. phys. Chem., ix, 338, 1892.

solubility,* and renders the solutions supersaturated as soon as they are out of contact with the compressed solid. This is merely another statement of the fact that on straining a crystal its solubility on the strained face is increased; consequently a strained crystal in contact with a saturated solution in any solvent dissolves on the strained faces, and is redeposited where there is no strain. The effect of this is that the crystal changes in such a way as to diminish the strain on it—an example of the well-known principle that the readjustment of a system following disturbance of the equilibrium is always such as to minimize the effect of the disturbing factor.

Le Chatelier accounts in this way for the solidification of natural beds of rock-salt, gypsum, calcium carbonate, and clay. To test this matter directly he compressed sodium chloride or sodium nitrate in contact with its saturated solution to about 200 atmospheres for a period of eight days, and found that blocks resembling rock-salt and marble were formed in this way. Somewhat earlier than this, Spring† had made analogous experiments, compressing to about 6000 atm. a great variety of substances, previously powdered and moistened with a few drops of water. He found that the metals would not weld together until the water was squeezed out; with most other substances compact blocks were obtained. Even with very slightly soluble substances—e. g., calcium carbonate—the effect of the water was noticeable, as the blocks obtained in this way from the moistened powder were more compact than those resulting from compression of the dry powder.

Now, uniform pressure (acting on both solid and liquid), *increases* the solubility of those substances the dissolution of which is attended with a *decrease* of total volume; consequently uniform pressure is sufficient to account for the consolidation of substances belonging to this category. But uniform pressure will not account for the consolidation of those substances the dissolution of which is attended with an increase of volume; whose solubility, therefore, diminishes with increase of pressure. Unequal pressure (acting in excess of the solid phase) is competent to account for the consolidation in all cases excepting one relatively infrequent case: namely, with substances belonging to the second category, when ΔP is small compared to P (see footnote, p. 213). This case apparently occurred with two substances tried by Spring, for he states that ammonium chloride and potassium iodide gave friable blocks, much softer than those obtained by compressing the dry powders. Spring

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*The amount of this increase of solubility can be computed by equations in every respect analogous to those applicable to the effect of pressure on the melting point.

†Zs. phys. Chem., i, 532–5, 1888; Ann. soc. géolog. Belg., xv., 156, 1888.

considered his pressure uniform, and gives an explanation on that basis, essentially similar to that above. From his mode of experiment it is obvious that his pressures may have been so nearly uniform that the inequality of the pressure on solid and liquid was not sufficient to effect an absolute increase in the solubility of the above two substances. Under geological conditions it is probable that such a case is exceptional, firstly because there are relatively few substances belonging to the second category above, and secondly because even with these substances it can occur only under specified, and to some extent exceptional, conditions of compression.

Another piece of evidence may be cited from Spring, who writes* as follows: We may suppose "that the component sand grains of sandstone, or the rolled pebbles of pudding-stones, have been in contact with a supersaturated solution of silica produced by the agency of pressure, and that this solution, in unstable equilibrium, [that is, wherever the pressure is released] has furnished the cement necessary for consolidation. It is not without interest to determine if there really exists between the component granules a silicious material which escapes direct observation. Now dry amorphous silica has the property of dissolving slowly in a solution of alkali hydroxide, whereas quartz grains are refractory or are attacked by alkali only with extreme slowness. A block of sandstone or of pudding-stone ought then to be disintegrated in a solution of potash, if there is really a layer of silica, however fine, between the grains. Experiment has confirmed this deduction : all the quartzose or schistose rocks which have been examined have disaggregated in an alkaline liquid, but with greater or less rapidity according to their nature. Sandstones of relatively recent formation, such as tertiary sandstones (landéniens) or secondary sandstones (keupriques), have required only some weeks at 100° to be disaggregated, while older sandstones, psammites and especially pudding-stones, have been much more resistant to alkalies. The latter become only more or less friable, whereas the former were changed into mobile sand. The reason for this greater resistance is obvious. In all probability it consists in the circumstance that the silica which cemented the grains together has in the lapse of time been transformed into quartz, which is refractory towards alkali."

This view is confirmed by a few experiments made by Spring, which showed that sand grains may be cemented together by keeping them under slight pressure in contact with colloidal silicic acid, while the latter slowly dried.

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* Bull. Acad. Roy. Belg. (3), xxxvii, 810-12, 1899.

CORRELATION OF MECHANICAL PROPERTIES OF METALS WITH THE (UNEQUAL) PRESSURE REQUIRED TO DEPRESS THEIR MELTING POINTS TO ORDINARY TEMPERATURE.

Further corroboration of the plausibility of the view that unequal pressure is effective in correlating phenomena attending the deformation of crystalline solids is afforded by a consideration of the parallelism observed between the calculated melting pressures (ϕ) at ordinary temperature and certain of the mechanical properties of metals.

The (unequal) pressure (ϕ, expressed in atmospheres) required to cause a substance to melt at the temperature T_2 can be computed if we can integrate equation III. We cannot perform this integration rigidly for lack of the necessary data on the variation of ΔH and V_s with pressure and temperature; but fortunately the variation of $V_s/\Delta H$ is small and for the present purpose unimportant. We may therefore consider $V_s/\Delta H$ to be independent of pressure and temperature: by integration and transformation we then obtain the equation

$$\phi = 95{\cdot}1 \ QD \log \frac{T_1}{T_2} \qquad \text{(V)}$$

which gives the melting pressure (ϕ) at the temperature T_2 in terms of the heat of melting (Q, in calories per gram) the density D and the ordinary melting point at one atm. pressure (T_1 in absolute measure).

At the present time the requisite data for the calculation of ϕ are available only for a few metals; these calculations have been made, and the results are presented in Table II. This and the following table are taken from another paper,* in which the results are discussed at some length. We shall therefore recapitulate the discussion only in so far as it is germane to the present subject.

The sequence of the metals when arranged in the order of their ϕ values (as calculated by equation V) is identical with that obtained when they are arranged in the order (1) of their flow pressures† (2) of the following mechanical properties‡;

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* Johnston, J. Am. Chem. Soc., xxxiv, 788–802, 1912; Zs. anorg. Chem., xxvi, 361–79, 1912. A preliminary note embodying the main conclusions appeared in J. Washington Acad. Sci., i, 250, 1911.

† As observed both by Tammann, Verigin and Levkojeff (Ann. Phys., x, 649, 1903) and by Kurnakov and Zhemzhuzhny (Zs. anorg. Chem., lxiv, 174, 1909). The amount of compression required to cause a material to flow is characteristic of the material under specified conditions; but at constant temperature it varies, as is obvious, with the size of the aperture through which the flow takes place; probably also it depends upon the shape of the aperture and upon other subsidiary factors. Hence determinations of flow pressures are not comparable, except they have all been made in the same apparatus and in the same way. This condition is fulfilled by the experimental observations cited, which lead to reliable relative values of the flow pressure for a series of metals.

‡ The values of these were collated and averaged largely from the Landolt Börnstein-Meyerhoffer Tabellen (2 Aufl. 1905).

Table II. Lowering of Melting Point of Metals effected by one atm. unequal pressure; together with the computed melting pressures at ordinary temperatures.

Metal	Melting point		Heat of fusion	Density	ΔT_1*	ϕ_{27}†
	t	T_1	Q	D		
K	62	335	15·7	0·87	0·59	64
Na	97	370	31·7	0 98	·29	266
Pb	327	600	5·4	11·37	·24	1760
Sn	232	505	14·1	7·29	·12	2200
Bi	270	543	12·5	9·80	·11	3000
Cd	321	594	13·7	8·64	·12	3300
Al	658	931	42·	2·60	·21	5100
Zn	419	692	28·	7·1	·084	6900
Ag	960	1233	23·	10·50	·12	14000
Cu	1083	1356	43·	8·93	·086	24000
Pd	1550	1823	36·3	11·4	·11	31000
Pt	1755	2028	27·2	21·5	·084	46000

*This column, which represents the melting point depression produced by one atm. excess pressure acting on the solid, is given merely to exhibit the magnitude of this quantity The values given are calculated from the formula

$$\Delta T_1 = \frac{T_1}{41{\cdot}30\ Q\ D}$$

which is easily derived from equation III.

†It should be observed that the values of ϕ given in the preliminary note (J. Washington Acad. Sci., i, 260, 1911) were calculated by a formula which holds strictly only so long as either ϕ or the difference between T_1 and T_2 is small. The more accurate mode of calculation from equation V of the present paper leads to somewhat higher numerical values of ϕ, but does not alter the order of the ϕ values; so that this change does not affect the argument.

(*a*) tensile strength, elastic limit, hardness; (*b*) compressibility, elastic modulus, rigidity modulus; as is shown by Table III. The exceptions to this statement are very few as regards any one property, and vary irregularly as we pass from one property to another; in other words, there are no systematic deviations between the sequence of the ϕ values and that obtained when the metals are arranged progressively with reference to any one of their mechanical properties for which measurements have been made. The slight divergences are no greater than one might expect from the uncertain character of the thermal data, on the one hand, and of the elastic constants on the other.

This remarkable concordance establishes the fact that the mechanical properties of metals are in some way correlated

TABLE III. Relative Values[1] of the Elastic Constants of Metals.

Metals in order as in Table II	Compressibility (*a*)	Hardness (*b*)	Tensile strength		Elastic Limit			Elastic (Young's) Modulus (*g*)	Rigidity Modulus	
			(*c*)	(*d*)	(*e*)	lower (*f*)	upper (*f*)		(*h*)	(*i*)
K	31·5	0·5	--	---	--	---	----	---	--	---
Na	15·4	0·4	--	---	--	---	----	---	--	---
Pb	2·2	1·5	2·0	21	0·3	25	102	17	5	0·80
Sn	1·7	1·8	2·1	36	4	34	55	34	16	1·50
Bi	2·8	2·5	--	---	--	---	----	32	12	---
Cd	1·9	2·0	--	48	--	28	109	71	17	2·31
Al	1·3	2·9	--	---	--	283	600	70	29	2·55
Zn	1·5	2·5	13	---	10	125	770	78	31	---
Ag	0·84	2·7	22	272	12	---	----	70	39	2·67
Cu	0·54	3·0	25	316	12	203	2780	108	42	4·37
Pd	0·38	4·8	--	---	27	---	----	103	46	---
Pt	0·21	4·3	29	---	26	---	----	161	52	6·46

[1] It is to be noted that the values given in the table are *relative* only, and are not always expressed in the same units (e. g., columns *c* and *d*, *e* and *f*, *h* and *i*).

a. As given by Richards and collaborators, J. Am. Chem. Soc., xxxi, 156, 1909.
b. According to Rydberg, L.-B.-M. Tabellen, p. 57.
c. L.-B.-M. Tabellen, p. 53.
d. Wertheim (1848) quoted by Faust and Tammann. Zs. phys. Chem., lxxv, 118, 1911.
e. L.-B.-M. Tabellen, p. 53.
f. As determined by Faust and Tammann, loc. cit.
g, *h*. General mean of the (sometimes very discordant) values given in L.-B.-M. Tabellen, pp. 43–45.
i. Horton, Phil. Trans. Roy. Soc. London, A, cciv, 1905.

with the pressure—assumed to act on the solid alone—required to cause the metal to melt at, or about, the ordinary temperature; and suggests that the "flow" of metals—or indeed every *permanent* distortion of a crystalline* aggregate—is due to an actual fusion (with subsequent resolidification) of some of the particles.

The validity of this view is supported by a large number of well-known facts, e. g., that any metal requires progressively less effort to cause it to weld—or to forge it—as its temperature is higher; indeed this mode of accounting for "flow" has been employed more or less unconsciously by a large number of people as an approximate explanation of a number of common observations such as the above. It is corroborated by

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* The formula is obviously inapplicable to glasses or other supercooled liquid; for in such cases Q is zero.

a large number of observations, which demonstrate the existence of important differences between metal which has "flowed," or has been subject to deformation of any kind, and the same metal in the annealed condition. All the available evidence* goes to show that there is: (*a*) a difference in the energy content of the strained and unstrained metal, which is manifested in a difference between the two forms (1) in their electrolytic potential when immersed in a solution, (2) in their thermoelectric power, (3) in their heat of solution ; (*b*) a difference in structure, manifested in differences in (1) microscopic appearance, (2) mechanical properties—hardness, tensile strength, etc., (3) density,† (4) conductivity for heat or electricity, etc. For any one metal these differences vanish about a single temperature common to all—that is, at the temperature at which annealing proceeds with appreciable rapidity.

According to Beilby,‡ the process of deformation is always attended by a partial transformation of the metal into an "amorphous"§ form ; according to Faust and Tammann,‖ on the other hand, the change of properties on deformation is parallel to the production of smaller crystallites. Whichever be the correct interpretation—if indeed these views are mutually exclusive—the fact remains that deformation of a metal is attended by changes in its properties. These changes are such that they would be difficult to account for reasonably, except by the very simple supposition that an actual melting has occurred.

Further evidence in support of the view here advocated is presented in the paper above referred to ; enough has been presented here, we hope, to demonstrate the plausibility of the idea that any permanent deformation of a crystalline substance is determined by an actual melting of some part of the material—a melting which occurs as soon as the local stress reaches the melting pressure corresponding to the temperature of the material.

In what follows we shall make use of this conception to interpret the observations of those who have investigated the effect of high pressure upon solid systems : and hope to demonstrate that by the use of well-known criteria in conjunction with this conception the various observations can be reconciled ; which will enable us then to give a consistent account of the present status of the question.

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*Cf G. T. Beilby, Phil. Mag. (6), viii, 258–76, 1904, who discusses the evidence in detail

† These differences have been discussed in detail by the authors in a previous paper. J. Am. Chem. Soc., xxxiv, 563, 1912.

‡ Loc. cit.

§ Beilby here uses the term "amorphous" to denote a heterogeneous assemblage of molecules.

‖ Zs. phys. Chem., lxxv, 108–26, 1911.

The possibility of accounting for the flow of solids by means of this conception of a true local melting produced by unequal pressure was considered by Tammann,* but rejected by him on what appear to the writers to be insufficient grounds. He was unable to detect any discontinuity in the rate of flow of ice at the pressure calculated by means of the equation for the lowering of equilibrium temperature by unequal pressure, and hence was led to doubt the thermodynamic admissibility of the derivation of this formula. To reason from this lack of discontinuity that the effect of unequal pressure upon the melting point is illusory, might be justifiable if Tammann had been dealing with a single crystal; but dealing as he was with an aggregate of crystals, flow began whenever the pressure on any one of them exceeded the melting pressure under the particular conditions. Indeed the behavior of ice in this respect is precisely similar to that of the metals—a fact specifically noted by Tammann himself—the only difference being that the absolute values of the pressure are lower than for the common metals.

Tammann concludes:† "From the work on the velocity of flow of crystalline substances it follows that the flow is not conditioned by a previous melting, but that the *plasticity, the reciprocal of the viscosity, is a property characteristic of the substance.*" In order to account for the fact that the velocity of flow, and hence the "plasticity," of ice increases very considerably with the pressure, it must be assumed that its viscosity diminishes greatly with pressure. This assumption may hold, for water at low temperatures and low pressures is an exception to the general rule that the viscosity of liquids is increased by pressure;‡ to the writers, nevertheless, it seems less forced to account for the flow by the aid of the considerations advanced in this paper; namely, that flow is the result of a partial melting. On this basis we can readily see why increased pressure, which causes more ice to melt and hence increases the amount of water present, should increase the plasticity. Moreover, so far as we have been able to ascertain, this explanation conflicts with none of the recorded observations on the flow either of ice of any other substance. Indeed, it receives direct confirmation from some recently published work of Hess on the plasticity of ice§: he found, as Tammann previously had also observed, that at a given temperature a considerable movement of the plunger takes place under a pressure much lower than that deduced thermodynamically

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* Ann. Phys. (4), vii, 198, 1902; Krystallisieren und Schmelzen (Leipzig 1903). pp. 173–181.

† Loc. cit.

‡ R. Cohen, Ann. Phys., xlv, 666, 1892; Hauser, ibid., v, 597, 1901.

§ Ann. Phys., xxxvi, 449–93, 1911.

(on the assumption that the pressure acts equally on both the ice and the water produced by the melting), and presents indisputable evidence that the ice in these circumstances had actually melted.

The foregoing discussion of the general effects of compression on crystalline aggregates accentuates the importance of the distinction which must be made between two types of compression, viz., according as the pressure is uniform in character or otherwise; if the compression is not uniform, there is more or less deformation—which, on the views here advocated, is conditioned by an actual melting of a part (and probably only a very small fraction) of the material—and the magnitude of the effects produced is many times greater than when we are dealing with uniform pressure.

THE EFFECT OF COMPRESSION OF ONE-COMPONENT SOLID SYSTEMS.

A.—*The Flow of Solids under Compression.*

Spring, in an early paper* entitled "Researches on the property which solid bodies possess of welding (*de se souder*) under pressure," describes in detail work with a large number of substances of varied character, many of which he was able to cause to flow.† This expression was understood by W. Hallock‡—and since then by others—to signify a fusion, or true melting, of the whole mass of the solid; and accordingly he performed experiments to disprove what he conceived to be Spring's claim. For instance: Spring states that at 700 atm. beeswax flowed out of his apparatus like water, and at 2000 atm. paraffin flowed very easily. Hallock took cylinders of wax and paraffin, in which were imbedded pieces of lead and other metals, and subjected them to a pressure of 6000 atm.; but he found that everything came out just as it went in. "Nowhere was there a sign of true liquefaction. The wax and paraffin had acted only as viscous solids, and flowed only to fill the available openings."

Shortly afterwards Spring§ published a note, in which he pointed out that his language had been misinterpreted by Hallock, whereupon the latter admitted the justice of this protest.‖ But this contributed nothing towards reconciling the

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* Bull. Acad. Roy. Belg. (2), xlix, 323–79, 1880; Ann. chim. phys. (5), xxii, 170, 1881.

† These observations, together with others, are tabulated in summary form below (p. 225).

‡ W. Hallock, this Journal, xxxiv, 277–81, 1887; U. S. Geol. Survey, Bull. 55, 67–75, 1888.

§ Bull. Acad. Roy. Belg., xiv, 585, 1887; this Journal, xxxv. 78–9, 1888.

‖ This Journal, xxxvi, 59–60, 1888; U. S. Geol. Survey, Bull 64, 38–9, 1890.

observations recorded by the two men. This inconsistency is easily removed as soon as we consider the forms of apparatus used, and the mode of compression possible in such apparatus.

Spring's apparatus—the same which was used in nearly all of his work—consisted essentially of a thick-walled steel cylinder, cut in a plane parallel to the axis into two parts which were held together by a screw; in this cylinder a hole 8^{mm} in diameter was bored. The piston was actuated by a lever on which weights were hung*; from the total weight, the ratio of the arms of the lever, and the cross-section of the piston, the amount of the compression was calculated. But the piston used was not a good fit for the cylinder: Spring in one instance says that the play between piston and cylinder was "kaum einige Zehntelmillimeter,"† and speaks repeatedly of the compressed substance as flowing out of the cracks (*fentes*) of the apparatus.

The form of apparatus used by Hallock consisted essentially of a thick-walled steel cylinder with a tight-fitting piston, actuated by an appropriate method. Experiments similar to those of Hallock have since been made by others, using analogous apparatus with a tight-fitting piston; with, of course, similar results.‡

The difference between the observations of Spring and those of later investigators is now easily accounted for. In Spring's experiments the compression was very far from being uniform, and part of the material squirted out round the piston; in other words, Spring made rough, but fairly comparable, determinations of the *flow pressure* of the materials, and was working therefore with "unequal pressure," as we have termed it in this paper. In the work of the other investigators the pressure was practically uniform, except perhaps for a few moments until the available space inside the bomb was completely filled with the material; hence, in conformity with the observations, no melting took place since, as we have seen, uniform pressure raises the melting point in general, and in the particular case of paraffin raises it by quite a notable amount. Indeed, one might say that, since uniform pressure tends to increase the rigidity or viscosity of substances, pieces of metal imbedded in paraffin or wax would be the less likely to change their positions the higher the pressure employed.

The difference between the modes of action of equal and unequal pressure accounts for the difference in the observations. With regard to a large number of substances, the

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* Or, in some experiments, by a screw.

† Zs. phys. Chem., ii, 535, 1888.

‡ For instance, by G. Spezia, "Some Presumed Chemical and Physical Effects of Uniform Pressure," Atti R. Accad. Sci. Torino, xlv, 1–16, 1910.

various investigators are in substantial agreement as regards the pressure requisite to consolidate the dry material. These pressures are in the nature of flow pressures, because they represent the force required to deform the individual particles and to cause them to flow or weld together. The actual magnitude of the observed welding pressures has little significance because it depended in all these cases upon a number of factors not under control; but it is worth while to make a rough classification according to the relative ease with which the dry substance welded at ordinary temperature. This is done in the following summary of results, taken mainly from the papers of Spring, Hallock, and Jannettaz;[*] in part also from scattered sources, including a few results obtained in this laboratory.

Summary of the Results on the Relative[†] *Ease of Welding of Various Substances.*

(*a*) *Hard and compact blocks* were produced by pressure: with all the metals investigated (including bismuth and antimony): with NH_4Cl, $NaCl$, KCl, KBr, KI, KNO_3, $NaNO_3$, $PbCl_2$, $HgCl_2$, HgI_2, ZnS, PbS, As_2S_3, MnO_2, $AlPO_4$;[‡] with oxalic acid, sulphur, graphite; with wax, paraffin, and similar substances; with camphor, resin, starch, and peat.

(*b*) *Soft and easily destroyed blocks* were obtained (using pressures up to 10,000 atmospheres) with: red phosphorus, HgO, HgS, FeS, $Al_2(SO_4)_3$, $CaSO_4$, (dry) Na_2CO_3, $ZnCO_3$, iceland spar, borax, sugar.

(*c*) *Very little or no effect* was observed with: amorphous carbon, silica, alumina, magnesia, powdered glass, chalk, $PbCO_3$, dry cotton.

In the above summary there is some doubt as to the class in which certain of the substances should be placed; besides which there is, of course, no sharp line of demarcation between the classes. All are in agreement, however, that with the highest pressures hitherto attained in such work (15,000 atm.) absolutely no effect is produced with *dry* silica, alumina, magnesia, or powdered glass. With the exception of the glass (which being a subcooled liquid has no melting-point) these substances are precisely those which, of all the substances mentioned above, melt at the highest temperatures. Further examination of the above summary demonstrates the existence of a

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[*] Bull. soc. chim., xl., 53, 1883: Bull. soc. géol. France (4), xii, 227–36, 1884.

[†] Because of the very approximate character of the data, no effort has been made to arrange the substances in each group according to the ease with which they weld together.

[‡] Furthermore, with hydrated salts and with many salts when moist; in connection with this see p. 216.

rough parallelism between relative ease of flow and melting point, namely: that a substance can be welded more easily the lower its melting-point; to this point we shall revert later.

EXPERIMENTAL INVESTIGATIONS OF THE EFFECT OF (NON-UNIFORM) COMPRESSION ON SOLID BLOCKS OF MINERALS AND ROCKS.

A large number of papers dealing with the behavior of solid blocks of minerals and rocks when exposed to compression have been published. Most of these are of interest only in connection with the compressive strength* of rocks (e. g., for use as building material) and hence need not even be referred to here; several, however, which have a direct bearing on the question under discussion will be treated briefly.

The general procedure adopted in these investigations was that suggested originally by Kick. If the material was a crystalline aggregate, it was fashioned into a cylindrical block which was inclosed in a tight-fitting steel tube by heating the latter and shrinking it on to the material. When separate crystals were employed, they were placed in a piece of stout copper tube of suitable size and the interstices filled up with an embedding material—e. g., sulphur, fusible metal, alum, or paraffin wax—which at the end of the experiment was removed by solution in water or by fusion. In either case the pressure was applied to the two ends of the metal tube, and continued in gradually increasing amount until considerable deformation of the tube and contents ensued. From the mode of experiment it is obvious that the compression was never uniform, and became less and less uniform as the strength of the supporting tube became less. This is the main disadvantage of the method, for it is impossible to arrive at more than a very rough approximation in an endeavor to estimate the amount of pressure in any direction; consequently qualitative results only can be obtained by this means.

The most extended investigation along this line is one by Frank D. Adams,† who worked with a series of minerals of varying hardness, as follows: selenite (2), rock salt (2·5), iceland spar (3), fluorite (4), apatite (5), diopside (5·5), limonite (5–6), orthoclase (6), magnetite (5·5–6·5), pyrite (6–6 5), quartz (7), garnet

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* The compressive strength of rocks, its variation with the mode of compression, and the precise significance (or lack of significance) of such results in relation to the question of the depth of the "zone of flow" in the earth's crust are ably discussed in two recent papers, one by F. D. Adams (J. Geology, xx, 97–118, 1912), on the experimental side, the second a mathematical discussion by L. V. King (ibid., 119–138).

† "An Experimental Investigation into the Action of Differential Pressure on Certain Minerals and Rocks, employing the Process suggested by Professor Kick" (J. Geology, xviii, 489–505, 1910).

(6·5–7·5). The tests, which were made with approximately equal final loads and under ordinary conditions of temperature, showed in general that the harder the mineral the less plastic it is; the hardest of the minerals were reduced to powder which did not weld together again. The softer minerals showed marked change of shape but appeared as coherent blocks often traversed by series of fissures: in the regions of greatest deformation they had become translucent or even nearly opaque, and in the case of fluorite there was moreover a marked change of color. The compression produced some twinning in the iceland spar, and in the diopside crystals it developed a series of polysynthetic twin lamellæ.

Adams also worked with several rocks—marble* from Carrara, several limestones, dolomite, and biotite granite—and found that their behavior is altogether analogous to that of the minerals. The softer rocks are readily deformed, the movement taking place in part by distortion of the mineral grains and in part by the development of a cataclastic structure, but in the main they tend to crumble to powder.

Precisely similar investigations had been published some years earlier by Rinne,† whose observations are entirely concordant with those of Adams; the comparatively soft rock salt and sylvite (KCl) were deformed into translucent blocks, nearly free from cracks and fissures.

Adams and Coker‡ have made similar tests with marble at temperatures of 300° and 400°, and also with marble at 300° in presence of water. Their observations show that the flow takes place with greater ease at the higher temperatures; its character is identical with that observed at ordinary temperature, and is not affected appreciably by the presence of water. They found moreover that the compressive strength of deformed marble depends upon the rate of deformation and the temperature, being greatest when the deformation is produced slowly and at higher temperatures, and increases to some extent if weeks or months intervene between the deformation and the test.

These observations can all be coördinated satisfactorily with one another, and with the observations on the relative ease of

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* Cf. also: Frank D. Adams and J. T. Nicolson, "An Experimental Investigation into the Flow of Marble," Phil. Trans. Roy. Soc. London, A, cxcv, 363–401; F. D. Adams and E. G. Coker, "An Investigation into the Elastic Constants of Rocks, especially with Reference to Cubic Compressibility," Carnegie Institution of Washington, Pub. No. 46, 1906.

† F. Rinne, "Beitrag zur Kenntniss der Umformung von Kalkspathkrystallen und von Marmor unter allseitigem Druck," Neues Jahrbuch für Min., 1903, i, 160–78; "Plastische Umformung von Steinsalz und Sylvin unter allseitigem Druck," ibid., 1904, i, 114–22.

‡ F. D. Adams and E. G. Coker, "An Experimental Investigation into the Flow of Rocks. I. The Flow of Marble," this Journal (4), xxix, 465–87, 1910.

welding (p. 225), if we look upon the net effect as a breaking down or crumbling of the crystals by the compressive force, accompanied by a simultaneous (and, perhaps, also a subsequent) welding together again of the grains produced in this way. This way of regarding the phenomenon is supported by the following observation: a small quantity (about 0·7 grams) of finely powdered dry salt (NaCl) was placed in a steel bomb with a hole, 1/2 inch in diameter, into which a hardened steel plunger fitted tightly, and was by this means subjected to a pressure of some thousands of atmospheres; after being compressed it appeared as a button, 13^{mm} in diameter and 3^{mm} thick, which was sufficiently transparent to enable one to read print through it.* Thus this observation shows that, starting with a substance in the form of fine powder, we can by applying sufficient compressive force obtain a block of material altogether similar to that produced by the deformation of a single crystal of the same substance.

None of these observations on the effect of differential stress on crystals and crystalline aggregates conflict with the idea that permanent deformation is conditioned by a real local melting. Indeed many of the observations directly support this idea: thus, for instance, the production of twinning on deformation, as noted by Adams, would seem to be more easily accounted for by considering that an actual partial melting had occurred than by ascribing it to the operation of purely mechanical factors; and again, substances exhibit greater plasticity the higher the temperature. Moreover we note again that there is a general parallelism between relative ease of flow and melting point, a parallelism which is precisely what we should expect if an actual local melting takes place during the process of flow of a solid.

Correlation of the Relative Ease of Flow with Physical Constants of the Material.—The conclusion that there should be a parallelism between relative ease of flow and melting point, although almost obvious from general principles, can be derived readily from equations III or V. For, according to the views advocated in this paper, the ease of welding is parallel to the ϕ value, which in turn depends upon the density, heat of melting, and temperature of melting. Now of these three factors, the first lies within comparatively narrow limits for a series of substances, and especially for a series of minerals; the second is not known, but probably lies also between comparatively narrow limits *in general*;† the limits within which the melting point lies are comparatively much

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* A similar observation has been made previously by some one else (probably by Spring), but we have been unable to locate the reference.

† The exceptional cases would be those in which the heat of melting is very small.

wider apart. Consequently, as a first approximation, we should expect the existence of the parallelism noted above.

It may be noted, in passing, that the possession of really comparable quantitative data on the actual flow pressure of a series of substances in combination with data (densities and melting-points) which are either already known or easily obtainable, would probably enable us to predict the magnitude of the effect of pressure on the melting point. For by collating the experimentally determined flow pressure with the value of ϕ calculated for those substances for which the necessary data exist, we could determine the relation between ϕ and the experimental value, and then by means of this relationship compute, for other substances, ϕ and the effect of pressure—either uniform or unequal—upon the melting point; moreover, we should then be able to compute the latent heat of melting as soon as we knew the density and melting point, both of which quantities can be determined with ease and accuracy. A further point is this, that there is a pronounced parallelism between hardness (as ordinarily measured) and the ϕ values, hence between hardness and melting-point; it might, therefore, be possible to devise a method of measuring hardness from which approximate knowledge of the change of melting-point with pressure—or even the latent heat of melting—could be derived.

Closely related to the question of the flow of solids produced by compression is that of the effect of pressure on viscosity: this we shall consider very briefly.

The Effect of Pressure on Viscosity.

The effect of pressure on viscosity has up to the present been studied to but a slight extent; and the investigations recorded are concerned with a very few liquids, the viscosity being measured by the usual transpiration method, in a slightly modified form of apparatus. Warburg and Babo* found that an increase of pressure from 70 to 105 atm. caused an increase of about 30 per cent in the viscosity of liquid carbon dioxide. Later Warburg and Sachs,† working at pressures up to 150 atm., found that while pressure increased the viscosity of ether, benzene and liquid carbon dioxide, it decreased that of water,—an unexpected result which had previously been obtained by W. C. Röntgen.‡ R. Cohen§ investigated the effect on water and certain aqueous solutions of sodium chloride, and on turpentine, over a range of pressures extending up to 600 atm., and at temperatures between 0° and 30°; and found an increase of viscosity with pressure in the case of the more concentrated

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* Ann. Phys., xvii, 390, 1882.

† Ibid., xxii, 510, 1884.

‡ Ibid., xxii, 518, 1884.

§ Ibid., xlv, 666, 1892.

salt solutions and turpentine, but a decrease with water and with the weaker solutions at the lower temperatures. The variation in the case of water is not proportional to the pressure, and is greater at the lower temperatures, but Cohen did not observe a minimum viscosity. These results were confirmed by Hauser,[*] who investigated the viscosity of water at pressures up to 500 atm. and temperatures up to 100°. He found that the effect reached a minimum at 32°, at which temperatures a pressure of 400 atm. was without effect on the viscosity; above 32° pressure causes an *increase* in the viscosity of water.

All the available evidence indicates, therefore, that the effect of pressure is to increase the viscosity of liquids. The anomalous behavior of water at low temperatures is in line with its abnormal behavior in other directions, and is, in all probability, altogether exceptional.

Röntgen[†] also investigated the effect with marine glue,[‡] a substance which behaves as a very viscous liquid or as a brittle solid according to the character of the forces to which it is subjected. He made parallel experiments on the penetration of a block of the material by a loaded rod (a) at 1 atm., (b) at 500 atm., and found that its viscosity increased under compression, but regained its original value when the pressure was removed.

These comprise, so far as the writers are aware, all the investigations dealing with this question; they show that the effect of uniform pressure is always to increase the viscosity (water and certain dilute aqueous solutions, both at low temperatures, excepted).

The question of the viscosity of solids is as yet by no means in a satisfactory state; but, for various reasons, we cannot discuss[§] it here. Suffice it to say that we have at present no accurate knowledge of solid viscosity[‖] (the term even is ill-

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[*] Ann. Phys., v, 597, 1901. [†] Ibid., xlv, 105, 1892.

[‡] Barus, using a transpiration method, measured the viscosity of marine glue at ordinary pressure and temperature, and found it to be of the order of 10^8 as compared with values of 10^{-2} for water and about 10 for glycerine, at ordinary temperature. (U. S. Geological Survey. Bull. 73, 134, 1891.) The brittleness of this substance, noticed when even moderately great forces are suddenly applied, is correlated with its high viscosity.

[§] The reader desirous of further information will find the earlier work (up to 1890) reviewed by Barus, in his bulletins on solid viscosity (No. 73 cited above, and No. 94, 1892; the greater part of this work appeared also in this Journal, and in Phil. Mag., 1888–1892). A recapitulation of the present-day status of the question will be found in text-books of elasticity, e. g. "The Mathematical Theory of Elasticity," either of Love (Cambridge University Press, 2d edition, 1905), or of Ibbetson (Macmillan); or in Winkelmann, "Handbuch der Physik" 2 Aufl. 1908.

[‖] In this connection it may be observed that any flow of a solid is accompanied by a change in its molecular configuration and in its properties; in all such cases, therefore, we are not dealing with an absolutely definite system. The same remark applies more or less to measurements of the tensile strength and analogous "constants" of metals.

defined) even at ordinary pressure. There is, however, no basis of any kind for the statement that high pressure causes a decrease in the viscosity of solids. It is true that stressed solids flow whenever the magnitude of the stress is sufficient to overcome the resistance to flow offered by the body; but all the evidence tends to indicate that this resistance to flow *increases* when the body is exposed to the action of high uniform pressure.

In view of the lack of definiteness of our present notions of solid viscosity and of the uncertainty as to the significance of the numerical data on viscosity of solids, it behooves us to exercise great caution in the use of the idea of viscosity in any argument dealing with solid systems. But our present inability to make advantageous use of the idea matters the less,—especially in applications to geological problems—because viscosity affects only the rate of change of the system, but not its final state. To quote the concise statement of Ibbetson:

"The amount of viscous resistance of a given solid or fluid, at a given uniform temperature, depends only upon, and increases continually with the *rate at which shear takes place*, and invariably *vanishes with this rate*:—or in other words, infinitely small resistance is offered by viscosity to infinitely slow moving.

"The existence of viscosity in a material does not therefore affect the conditions of *equilibrium* under stress, but only resists and modifies the process (other than simple [uniform] dilatation and compression) by which a body passes from one state of strain to another; a relation being introduced between the *magnitude of the stress* producing the change of state and the *time occupied* by the change.

"Although a fluid may, in virtue of its viscosity, offer immense resistance to *sudden* or *rapid* distortions, yet any shearing stress, however small, will suffice to produce any required amount of flow, however great, *provided that it be applied continuously for a sufficient length of time*."*

Residual Effect of Compression on the Density of Solids.

This question, which is closely related to the general question treated in this section, has been fully treated in another communication.† In this paper it is established that a residual effect—a *decrease* of density—is observed when, and only when, the material (supposed homogeneous, i. e. free from ordinary vacuoles or inclusions‡) has been subjected to deforma-

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* Ibbetson, *op. cit.*, p. 175. The italics are Ibbetson's.

† J. Am. Chem. Soc., xxxiv, 563–84, 1912; Zs. anorg. Chem., lxxvi, 274–302, 1912.

‡ It is obvious that any result might be obtained with a substance which does not satisfy these conditions.

tion. In the case of metals, this residual decrease of density after compression is closely connected with the changes of other properties produced by deformation, referred to elsewhere in this paper.

B. The Alleged Effect of Compression in Producing Crystalline Forms and in Effecting Transformations.

In the early paper previously referred to* Spring avers that on subjecting certain substances to compression a recrystallization or a transformation from the amorphous to the crystalline state had occurred. The changes which Spring claims to have effected in this manner are: the crystallization of bismuth, zinc (at 130°), manganese dioxide, the sulphides of zinc and lead, mercuric iodide, and the transformation of plastic and monoclinic sulphur to the rhombohedral form.

This conclusion was challenged by Friedel,† who failed to observe any trace of crystallization on compressing to 10,000 atmospheres the sulphides of lead or zinc. Somewhat later similar experiments were undertaken by E. Jannettaz‡ on a more extensive scale; he too failed to confirm Spring's deductions. Jannettaz states that in many substances pressure develops not crystallization but schistosity, the plane of which is perpendicular to the direction of pressure; this was demonstrated by the difference in heat conductivity in the direction normal to it. His conclusion is: "compressed powders do not crystallize; a large number of substances—e. g. metals, clays, graphite, steatite—under these conditions assume a schistose structure, and exhibit the thermal properties characteristic of this structure."

Spring,§ in reply to this, points out that he had not claimed that crystallization of a substance is a general consequence of compressing it; out of 83 substances examined, there were evidences of crystallization in only 7. In some of the cases he had expressly stated that pressure has little or no effect, in this respect agreeing entirely with the observations of Jannettaz. He points out the necessity of working with clean substances and in a vacuum, so that there may be no layer of foreign material between the grains to be pressed together, and attributes to neglect of this precaution both the failure of Jannettaz and Friedel to duplicate his results on crystallization and the schistosity noted by Jannettaz. According to Spring, schistosity is a secondary phenomenon, due to the interposition, between

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*Bull. Acad. Roy. Belg. (2), xlix. 323–79, 1880.
† Bull. soc. chim. (2), xxxix, 626, 1883.
‡ Ibid. (2), xl, 51, 1883.
§ Ibid. (2), xl, 520–5, 1883.

the solid particles, of foreign liquid or gaseous material which prevents the complete agglutination of the powder. Consequently, it can be produced at will by compressing in the presence of some gas or by having foreign matter on the particles.*

There remained four substances—bismuth, lead sulphide, zinc sulphide, and mercuric iodide—for which Spring's results conflicted with those of Jannettaz. In order to convince his opponents, Spring exhibited his specimens, and performed new experiments, in presence of Friedel and others, whereupon Friedel writes in part as follows:†

"The contradiction is more in the manner of expressing the results than in the results themselves, which are altogether comparable [with those of Friedel and of Jannettaz]. Nevertheless in certain cases in which Spring sees a crystalline condition, and where indeed evidences of crystallization may be detected with a microscope, I cannot admit that there has been crystallization as a direct consequence of the compression; that is to say, I cannot admit that several crystalline grains of the original precipitate have welded together so as to form a single crystal, traversed by continuous cleavage planes; one would then have a single visible crystal and not the structure actually observed, which can be denoted only by the term aggregate or microcrystalline structure, the crystalline grains being no larger than those in the original powder."

In only one case—metallic bismuth, which was squeezed out through the space between plunger and bomb—will Friedel admit a possible crystallization; the evidence for it rests only on the appearance of broken surfaces of the metal, and can hardly be regarded as showing that a process of crystallization has actually taken place as a result of the compression. In accordance with this, Friedel concludes that there was no marked crystallization by pressure under the conditions of Spring's experiment, though he does not doubt that it may occur in certain cases.

This conclusion is in harmony with present experience. Thus a substance—e. g. sodium chloride—which crystallizes in the regular system may be compressed from powder into a hard and fairly transparent block; yet microscopic examination of such a block, shortly after it had been formed by compression, showed that the original grains were merely stuck together—that an agglomeration, but no formation of larger crystals had occurred. Whether diffusion could in time pro-

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*The presence of water will in general not produce schistosity, for the reason that it dissolves to some extent the surfaces of the individual grains, and in this way tends to behave as a cementing agent. See p. 216.

† Bull. soc. chim. (2), xl, 526–8, 1883.

mote the formation of larger crystals in such a block is a question upon which there is at present no direct evidence.*

Similarly the blocks formed by compressing filings or grains of metal are, in general, agglomerates† of the original grains cemented together by layers of deformed or flowed metal around the edges; such blocks show considerable rigidity, by reason of this cementing action, and are stronger in proportion to the total deformation produced by the compression. This is in agreement with the well-known fact that the strength of metals increases when they are deformed in any way (as by hammering, rolling, or drawing to wire)—a fact which is in harmony with the ideas here enunciated regarding the phenomena resulting from unequal pressure and consequent flow‡ in the interstitial spaces.

We should, therefore, conclude that recrystallization will occur only in those parts (usually a small fraction of the whole amount of material) which have been subjected to compression sufficient to produce melting; and hence that the actual amount of recrystallization would be greater as the amount of deformation is greater and would be little or nothing at all when the compression is uniform—a conclusion which is in thorough accord with experiment. It is to be noted that the crystalline form which appears is that which forms under the particular conditions of temperature and pressure which obtain, and is not necessarily the form which would appear under normal circumstances.

With regard to the transformation of plastic sulphur into orthorhombic sulphur (the stable form under ordinary conditions) Spring's statements may be quoted in full.

" *Prismatic sulphur.*—Freshly prepared transparent prismatic sulphur was subjected to a pressure of 5000 atm. at a temperature of 13°. An opaque block, much harder than those obtained by melting, resulted. Microscopic examination of the fracture showed it to be identical with orthorhombic sulphur; from which one might suspect that the transformation of the prismatic into the orthorhombic form had occurred. In order to assure myself of this, I have found that the melting point of a fragment of the block formed by compression was 115°; now prismatic sulphur melts at 120°, orthorhombic sulphur between 111° and 114°. Moreover, the density of the block was 2·0156, whereas that of orthorhombic sulphur is 2·05 and that of the prismatic form is 1·96. These facts are in agreement as evidence of the transformation.

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*Cf. p. 248.

† Jannettaz, Bull. soc. chim., xl, 53, 1883; Hallock, U. S. Geol. Survey, Bull. 55, 71, 1889; Spezia, Atti Accad. Sci. Torino, xlv, 1–16, 1910.

‡ This matter is treated on page 219, and at length in the paper already referred to on p. 218.

Plastic sulphur.—Freshly prepared plastic sulphur supports a pressure of 3000 atm. without immediate modification, but is transformed in a few instants by a pressure of 6000 atm. This change begins before the pressure has reached 5000 atm. The surface of the block is then covered with a crust of orthorhombic sulphur, while the interior remains plastic." *

This evidence, while by no means conclusive, indicates that a certain amount of transformation had taken place. Indeed Spring, in a later article, admits this: "Yet this last transformation (that of plastic into orthorhombic sulphur) requires a long time. When the sulphur is taken out after being compressed for some hours, it is still soft in the central part of the cylinder. After undergoing compression for some days, the transformation is complete; although a sample of plastic sulphur, kept as a check under the same conditions of temperature, was not notably modified."†

The general conclusion to be drawn from this work is that compression alone will not in general produce crystallization or transform one modification of a substance into another; it will cause such changes in specific instances, where the conditions are such that the velocity of transformation is appreciable. The most important of these conditions are: (1) the character and magnitude of the compression; (2) the temperature of experiment in relation to the melting point of the substance; or perhaps more precisely, the amount of pressure required to cause the substance to melt at the temperature of experiment.

The effect of uniform (or even of nearly uniform) pressure is usually comparatively slight; for whereas uniform pressure will always tend to bring about any reversible (enantiotropic) change which is accompanied by a decrease of volume, it may not—and very often does not—do so because the reaction velocity under the specific conditions is not great enough. In other words, pressure brings about such changes in all cases in which the true equilibrium can readily be reached from either side; but if this is not so—either because the reaction velocity is inappreciable or because the transformation is irreversible (monotropic)—the condition produced is only an apparent equilibrium.

An exactly parallel case is the system hydrogen, oxygen and water at the ordinary temperature. We know that the true equilibrium in this system at ordinary temperatures is such that

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* Spring: Bull. Acad. Roy. Belg. (2), xlix, 351–2, 1880.

† Rapport Congrès Internat. de Physique, 1900. vol. i, p. 409. This article is a résumé of all of Spring's work up to that time. Of similar scope is a lecture reprinted in Bull. Acad. Roy. Belg. (3), xxxvii. 790–815, 1899. A résumé of this work has also been given by C. F. Tolman, Jr. (J. Geology, vi, 318-24, 1898), who, however, does not discuss it critically, but merely states the conclusions as given by Spring.

the quantities of hydrogen and oxygen are absolutely infinitesimal, and become appreciable only at high temperatures. On the other hand hydrogen and oxygen may be left in contact for a practically unlimited time, and show absolutely no signs of union; the reaction begins only at fairly high temperatures, when its velocity becomes appreciable.

This distinction between the theoretical state of equilibrium on the one hand, and the state actually attained under a given set of conditions and its dependence upon the reaction velocity under those conditions, on the other hand, is often lost sight of. Indeed, in a very large number of cases, we may say that the reaction velocity is the decisive factor in determining the final state, though of course the *direction* in which the reaction proceeds—if it proceeds at all—is determined by the energy relations of the various substances involved under the specific conditions of the experiment.

In some instances, so-called catalytic agents effect a great increase in the reaction velocity;[*] and some catalyst might be present in any system which was being compressed, and so bring about the reaction. But it appears unlikely that pressure itself will in general act as a catalytic agent. Whether pressure affects the reaction velocity in any direct way is a question upon which there is, so far as the writers are aware, practically no experimental evidence; but it is probable that its influence is generally negligible as compared with the enormous acceleration produced by change of temperature. It appears also that it may be in either direction, although only in a characteristic direction for any one reaction. In one case, the inversion of cane sugar by hydrochloric acid, Röntgen's experiments[†] indicate that a pressure of 500 atm. causes some diminution of velocity of this reaction.

The general conclusion stated above is in harmony with geological evidence. For instance, in nature glasses occur which are certainly less stable than the corresponding crystalline form; and we occasionally find intergrowths of two modifications of the same substance which cannot in general possess equal stability. Yet such cases occur in spite of the fact that the systems have been subject to compression—and even to some degree of temperature, in addition,—for geological periods.[‡]

As further direct evidence it may be mentioned that no

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[*] Thus palladium black brings about the union of oxygen and hydrogen around 100°.

[†] Ann. Phys., xlv, 100, 1892.

[‡] The fact may be recognized, however, that the older volcanic glasses have crystallized more or less completely; a fact which indicates that even under nearly ordinary conditions the process of devitrification can take place with extreme slowness.

pressure which we have been able to employ in this laboratory —and we have used pressures up to 15,000 atm.*—will convert calcite (sp. gr.–2·71) into arragonite (sp. gr.=2·93) nor marcasite (sp. gr.=4·9) into pyrite (sp. gr.=5·0); nor did the latter change take place to an appreciable extent at 425° under 2000 atm. pressure, although under ordinary pressure it does take place about 450°.† These cases are cited merely to show the folly of the statement that pressure will always actually produce the denser form. All that we may say is that, when the reaction is reversible (enantiotropic changes) pressure tends to displace the equilibrium in favor of the denser form, the actual appearance of which depends mainly on the velocity of reaction under the conditions involved; when the reaction is irreversible (monotropic changes, such as the two cases cited immediately above appear to be) we can make no positive statement as to the effect of pressure on the reaction, and can determine this effect for each particular monotropic change only by actual trial. The general statement may be hazarded that the influence of pressure on monotropic changes will be slight, with the important reservation that changes which we are accustomed to regard as monotropic may cease to be so and become enantiotropic when the system is exposed to high pressure. Apart from this, pressure can in all probability be effective only in changing the velocity of reaction, and, as we have seen, it is likely that this effect is small.

EFFECT OF COMPRESSION IN PROMOTING CHEMICAL REACTION BETWEEN SOLIDS.

Spring, in his first paper,‡ describes certain experiments on the occurrence of chemical action through the agency of pressure. Thus he states that copper and sulphur compressed to 5000 atmospheres react *completely* with the formation of black crystalline cuprous sulphide; that mercuric chloride and copper filings react under 5000 atmospheres to form cuprous chloride and mercury; that the mixture of mercuric chloride and potassium iodide, which is originally white, becomes red under 2000 atmospheres, all traces of the colorless salt having disappeared. On the other hand, nothing happened on compressing mixtures of potassium iodide and mercuric sulphide, mercury oxide and sulphur, or tartaric acid and sodium carbonate; but then these are reactions which would be accom-

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* This pressure is equivalent to a depth of about 34 miles below the surface of the earth, if we assume that the pressure at that depth is the weight of a column of rock the average density of which is 2·8.

† Cf. further the work of G. Spezia, referred to later (p. 247).

‡ Bull. Acad. Roy. Belg. (2), xlix, 323–79, 1880. An earlier paper, published in 1878, is merely a preliminary note.

panied by an increase in volume. The effect of this is, in Spring's experiments, not so important as it might seem to be; for any gas formed could easily escape between the piston and cylinder. Indeed this happened in one case at least, for he states that on compressing a mixture of sodium carbonate with arsenic oxide, much carbon dioxide was evolved, and a mass of sodium arsenate remained.

The bulk of the work along this line may be divided for convenience into three classes: these will now be considered separately.

A. THE FORMATION OF SULPHIDES AND ARSENIDES BY COMPRESSION.

In a later paper* Spring describes experiments in which the effect of repeated compression upon intimate mixtures of sulphur with a number of metals was investigated. The method was as follows: "The powder [obtained by mixing flowers of sulphur with filings of the metal] is submitted to a first compression of 6500 atm., whereupon it is transformed into a compact hard mass, microscopic examination of which shows that the reaction has taken place wherever the elements were in contact. This mass is then reduced to fine powder by means of a file, and this powder in turn is compressed again. This maneuver is repeated until the result is such that microscopic examination shows no trace of free metal or of free sulphur. Generally two or three compressions are sufficient to yield a perfect result; except that for the hard metals which have little affinity for sulphur, six or eight further compressions may be necessary." The results obtained, as given by Spring, are summarized in Table IV.

In another paper† he describes similar experiments resulting in the combination of arsenic with zinc, lead, tin, cadmium, copper and silver and the alleged production of homogeneous crystalline blocks.

Spring repeated certain of these experiments before Friedel, who writes:‡ "These experiments made before me by M. Spring prove that combination occurs between certain substances under the conditions under which he operates; that is to say, mixture of powders, compression, then pulverization again, followed anew by compression, and so on several times in succession. . . . For zinc sulphide, the change of color of the mixture seems to me a more certain indication of combination than the evolution of sulphureted hydrogen by the action of hydrochloric acid: for I have since found that

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* Bull. soc. chim., xxxix, 641–7, 1883; Bull. Acad. Roy. Belg. (3), v, 492–504; Ber., xvi, 999, 1883; Jahresbericht, 1883, 29.

† Ber., xvi, 324, 1883; Bull. Acad. Roy. Belg. (3), v, 229–36, 1883; Jahresbericht, 1883, 28.

‡ Bull. soc. chim., xl, 528, 1883.

TABLE IV. Spring's results on the formation of Sulphides by "compression."

Metal	No. of compressions	Result[1]
Mg	6	Gray mass, dissolves slowly in water at 50–60° with evolution of H_2S.
Zn	3	Block very closely resembling natural zinc blende.
Fe	4	Very hard homogeneous block, which could be filed only with difficulty.
Cd	3	Yellowish gray mass.
Al	5	Incomplete.
Bi	2	Perfectly homogeneous black mass.
Pb	-	Combine very easily.
Ag	8	Combination very slow, mass finally homogeneous.
Cu	3	Complete combination.
Sn	3	Grayish-yellow mass of SnS_2.
Sb	2	Gray-black mass resembling stibnite.
P	-	Absolutely no action.
C	-	Absolutely no action.

[1] In each case (excepting the two last) addition of acid to the product caused an evolution of sulphureted hydrogen.

powdered zinc and sulphur, mixed in presence of dilute hydrochloric acid, also give rise to an evolution of sulphureted hydrogen."

To these experiments the following observations may be made. For the formation of *some* sulphide of copper, or of other sulphides, it is not even necessary that the sulphur and copper be in contact. Thus Hallock* writes: "I have made the sulphide at ordinary temperatures with the copper and sulphur an inch apart and a wad of cotton in the tube between them. It is simply the *vapor* of the sulphur that attacks the copper. . . . The case of copper and mercuric chloride is precisely the same. The vapor of the chloride will go through a whole tube past cotton wads and attack the copper (or color potassium iodide)."

Now, in Spring's experiments the compression was far from uniform; hence the process of compression was accomplished by considerable grinding or kneading of the material, and so produced very good contact between adjacent particles. It is, moreover, highly probable that the process of reducing the compressed blocks to powder by filing also promoted combina-

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* Hallock, this Journal (3), xxxvii, 405, 1889.

tion by abrading the surfaces and bringing new surfaces into contact. There is also reason to doubt Spring's statement that some of the reactions had gone to completion; he applied no decisive chemical tests, but based his conclusion solely on the general appearance of the product (or of its fracture) when examined with the naked eye or microscopically—a criterion which cannot be regarded as very satisfactory for judging the extent to which a reaction has proceeded.

The general conclusion from this work is, therefore, that under the particular conditions of experiment combination between certain substances takes place to some extent; this, however, is practically a restatement of what has long been known, namely that grinding in a mortar will occasionally induce some degree of chemical action between solids. But we are in no wise justified in making the general statement that chemical action is promoted by compression, or *a fortiori* by uniform pressure; all that we may say is, that certain reactions are furthered by the close contact and grinding action produced by, and during, the application of compression; as soon as the compression has reached a steady value, action ceases except for the very slow diffusion which appears to be possible with certain systems and to be promoted by the intimate contact consequent on compression.*

From the standpoint adopted in this paper we should expect that the reactions most readily produced by compression would be those in which the melting point of the product is most easily depressed by the action of pressure. For the reaction will take place at the surfaces of contact but can proceed only so long as fresh surfaces continue to be exposed by removal of the thin layers of the reaction product formed at the contacts; this removal may be effected either by a melting, by direct mechanical abrasion, or by both combined. The evidence is at present too meager to admit of a demonstration of a parallelism between the extent of the reaction, and the properties of the reaction product; but at least it in no wise contradicts this idea.

B. THE ALLEGED REACTION BETWEEN SOLID SALTS.

1. *The Equilibrium:* $BaSO_4 + Na_2CO_3 \rightleftarrows BaCO_3 + NaSO_4$.

The effect of compression in promoting the above reaction between the *solid* substance has probably been quoted more often than any other part of Spring's work; and the results as stated by Spring (and quoted and re-quoted by others) have been used to support many geological speculations. The permissible conclusions from these results, however, differ con-

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* Cf. p. 248.

siderably from those usually quoted; consequently it seems advisable to consider these experiments in some detail.

Spring investigated first* the effect of repeated alternate compression and pulverization on the reaction between barium sulphate and sodium carbonate; and on the reverse action somewhat later.† He described his methods in the following words: "I have operated each time with about 1 gram of material [a mixture made by shaking together 1 part $BaSO_4$ (or $BaCO_3$) with 3 parts Na_2CO_3 (or Na_2SO_4), both powdered and thoroughly dried]. The small cylinder obtained by compression [to 6000 atmospheres] was then pulverized as fine as possible and the powder was washed completely with cold water. The insoluble residue, after being filtered off, was analyzed by the ordinary procedure in order to determine its content of barium carbonate." This process of alternate compression and pulverization was, with some changes, repeated a number of times in order to determine the effect of successive treatments; moreover, the cylinders after a given number of compressions were allowed to stand at atmospheric pressure for periods of time up to 28 days, and the amount of barium carbonate determined after treatment with water as above. The results are brought together in the following tables:

TABLE V. Percentage amount of $BaSO_4$ "transformed" into $BaCO_3$ (determined as above) by reaction with Na_2CO_3, under the stated conditions.

Number of "compressions"	Time of standing thereafter in days			
	0	7	14	28
1	0·94	1·60	3·08	3·84
3	4·78	6·78	9·01	9·15
6	8·99	9·94	10·89	11·08

TABLE VI. Percentage amount of $BaCO_3$ (determined as above) "transformed" into $BaSO_4$ by reaction with Na_2SO_4, under the stated conditions.

Number of "compressions"	Time of standing thereafter in days			
	0	7	14	---
0	49·79	48·95	49·47	----
1	59·16	63·91	64·66	----
3	69·25	74·98	77·38	----
6	73·31	80·68	80·31	----

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* Bull. soc. chim. (2), xliv, 166–9, 1885; Bull. Acad. Roy. Belg. (3), x, 204–8, 1885; Jahresbericht, 1885, 461.

† Ibid. (2), xlvi, 299–302, 1886; Jahresbericht, 1886, xxxix.

Attention is directed to the first line* of Table VI, in reference to which Spring writes as follows:

"When the mixture had been compressed for some instants to about 6000 atm., it was found that 59·16 per cent of the quantity of barium carbonate had been transformed into barium sulphate. This transformation is not, however, the exclusive result of compression; for the mixture obtained by shaking, but not yet compressed, when analyzed under the same conditions, furnished 49·79 per cent of barium sulphate. Moreover, simply by treating an identical weight of barium carbonate with a solution of sodium sulphate, the concentration of which was similar to that produced during the process of analysis, I obtained 40·29 per cent of barium sulphate. By taking account of these circumstances, one is led to the conclusion that simply shaking dry barium carbonate with sodium sulphate produced 49·79 − 40·29 = 9·5 per cent of barium sulphate; and that the process of compression in turn produced 9·37 per cent."

To all of this there is one fatal objection: namely, that it is absolutely useless to try to determine equilibrium conditions by means of any process which of itself disturbs the equilibrium. Therefore, the above results show only the relative amounts of the substances *after the addition of the water*, but can give us no certain information with regard to the actual state of equilibrium between the *dry* solid phases.

The truth of this reasoning is perfectly obvious, and so also is the inherent absurdity of the position that the equilibrium conditions between the solid phases may be ascertained by treatment with water. This is illustrated by the fact that a system composed of successive layers of powdered barium carbonate and sodium sulphate, when treated with water, would show considerable transformation,† although it is certain that the reaction between the *solids* under such conditions must have been absolutely inappreciable.

Now it is well known that the system,

$$BaCO_3 + Na_2SO_4 \rightleftarrows BaSO_4 + Na_2CO_3$$

when in presence of water, reaches in the lapse of time a state of equilibrium; indeed it was upon an experimental study of this equilibrium that Guldberg and Waage based the law of mass action. The condition of equilibrium is determined, in accordance with the law of mass action and the most generally

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* Similar control experiments with the reverse reaction showed that only a trace of $BaSO_4$ was transformed by simply shaking together the two powdered components.

† Indeed this is nearly identical with Spring's experiment in which he treated powdered barium carbonate with sodium sulphate solution, and found that 40 per cent of the carbonate had been transformed into barium sulphate.

accepted theory of solution, by the relative solubilities of $BaCO_3$ and $BaSO_4$ under the particular conditions of experiment, or in other words, by the relative concentrations of carbonate ion and sulphate ion in the solution. Equilibrium conditions are reached with comparative slowness; but in any given length of time—as, for instance, the time required to wash away the soluble material, as in Spring's method of analysis—the amount transformed would depend primarily on the intimacy of contact of the particles, and would tend towards the amount corresponding to equilibrium conditions. This then is sufficient explanation of the results of successive alternate compressions and pulverizations, and of the apparent limiting amount transformed ; as pointed out by Spring himself, "this result demonstrates the influence exercised by the renewal of the surfaces of contact of reacting substances upon the amount of the reaction product."

These observations then cannot be used as evidence in support of the contention that compression favors chemical reaction ; they do indicate, however, the possibility of interdiffusion of the solid substances after compression. Thus the tables show that the apparent amount transformed in the compressed blocks gradually increased with time ; this increase we attribute to more intimate mixture of the solid phases—for this would further the apparent extent of the reaction when water was added—and the most probable cause of this is to be sought in a slow process of diffusion* occurring between the grains which have been brought into intimate contact by the previous compression.

Before passing, one point remains to be noticed ; namely that the compressed cylinders heated for six hours to 160° showed less transformation than those not so heated. Now it would be easy to devise several hypotheses to account for this, but it is quite unnecessary to do so, because this shows only that on heating some factor intervened which influenced the contact between the particles, and because it can afford us no information whatever about the actual state of the *solid* system.

2. *The Reaction between Potassium Nitrate and Sodium Acetate.*

Equally unconvincing is the evidence for the reaction between solid potassium nitrate and sodium acetate.† Spring expected an interchange of bases and acids, and left the mixture of the dry fine powders for four months in a desiccator. On removing them from the desiccator a deliquescence was noticeable ; from which he concludes that the interchange had taken place, since the original salts do not easily deliquesce, but the product

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* Cf. p. 248.

† Spring, Zs. phys. Chem., ii, 537, 1888.

of the reaction (potassium acetate) does. Here again the equilibrium observed is that in the presence of water, and not that of the pure dry solids. In fact if the pure dry powdered salts are simply stirred together in the presence of water vapor, in a very few moments deliquescence begins;[*] so that the time factor is here of very secondary importance, if indeed it exerts any influence at all. This experiment again, therefore, offers no proof that any chemical change took place *before* the water vapor entered the system.

C. THE REPUTED FORMATION OF ALLOYS BY COMPRESSION.

By alternately compressing and filing down the compressed block, Spring[†] claims that he formed Wood's metal (from filings of bismuth, cadmium and tin in correct proportions), Rose's alloy (from lead, bismuth and tin), and with greater difficulty brass (from zinc and copper); his criteria for the formation of the alloy were solely the general appearance and the melting point of the specimens, neither of which can be regarded in any way as conclusive evidence of the actual formation of an appreciable quantity of the solid alloy. Similar experiments have been made by several later workers, none of whom reach conclusions in entire agreement with those of Spring.

Thus the melting point criterion was shown to be useless by Hallock.[‡] He made a mixture of filings of cadmium (1 part), tin (1 part), lead (2 parts), and bismuth (4 parts), and heated it to about 98–100°; in the course of a few hours a homogeneous liquid globule of Wood's metal had formed. Similarly an alloy formed on heating a piece of tin in contact with lead to about 200°; also when pieces of metallic potassium and sodium were put in contact at the ordinary temperature, in which case a thermoelement embedded in the potassium showed that the temperature fell and remained below that of the surroundings until reaction was complete. This behavior is exactly analogous to that of the freezing mixtures; for a salt and dry ice, both at $-10°$ or $-12°$, will combine rapidly. All of this shows that an alloy may be formed from its constituents by heating to a temperature above its melting point, though far below the melting points of its constituents.

This in itself does not directly settle the question at issue; but since that time all of those who have experimented along

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[*] Hallock, this Journal (3), xxxvii, 405, 1889; Bull. U. S. G. S., lxiv, 37, 1890.

[†] Ber., xv, 595, 1882; Bull. soc. chim., xxxviii, 549, 1882.

[‡] U. S. Geol. Survey Bull. 60, 147, 1890; Bull. 64, 34–37, 1890; this Journal (3), xxxvii, 402–6, 1889; Zs. phys. Chem., ii, 378–9, 1888.

this line have shown by direct metallographic evidence that no appreciable amount of a true alloy is produced by compression at temperatures below the melting point of the alloy.

Thus Rosenhain and Tucker* write: "Powdered lead and tin, mixed in the correct proportion of the eutectic composition, were compressed . . . pressures up to 35 tons per square inch (about 5000 atm.) being put on the metal. The small buttons of solid metal produced in this way were subsequently cut and polished for microscopic examination. . . . It will be seen at once [from the microphotographs, reproduced in the original] that the compound mass of metal can scarcely be regarded as a true alloy at all; the particles of lead and tin are merely juxtaposed and held together by surface cohesion. It is intended to observe these specimens from time to time, both when kept at the ordinary temperature and when maintained at temperatures just below the melting point of the eutectic, with a view to detecting the process of diffusion which will probably occur, but so far the time has been too short to allow of definite results being observed."

The same conclusion was reached by Spezia†, from analogous observations with copper and silver. The most thorough and detailed work along this line is that of Masing,‡ who in his introduction writes:

"The work of Spring was performed at a time when the structure of alloys had been little investigated. Now Rose's alloy is a conglomerate of crystals of the pure components, and it is only in such a case that one can expect that the crystalline conglomerates obtained by fusion and by pressure can be identical (except for certain secondary structural differences). This is highly improbable, however, when compounds or mix-crystals are formed on fusing together the components. We know that high pressure has in general little effect on the reaction velocity, and it is not to be expected that its influence on the rate of diffusion is very marked. Hence, it is impossible that notable amounts of compound or of mix-crystals should be formed in the course of a few hours by pressing together a mixture of powdered metals. There is therefore every reason to believe that in those cases in which mix-crystals or compounds appear the alloys obtained by fusion will differ considerably from the masses which result from compression."§

From this standpoint Masing investigated binary systems belonging to the three following types, with results which are summarized below:

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* Phil. Trans. Roy. Soc. London, A, ccix, 120–1, 1909.

† Atti Accad. Sci. Torino, xlv, 1, 1910.

‡ Zs anorg. Chem., lxii, 265–310, 1909.

§ Loc. cit., p. 266.

I. The metals crystallize as pure components from all their melts. Examples studied: Zn–Cd, Cu–Ag. In this case there is no essential difference between the conglomerates obtained by fusion and compression. There are, however, differences in structure; the former contains a lamellar eutectic, the latter is composed of irregular and irregularly distributed fragments of the components.

II. The metals form compounds, but no mix-crystals. Examples studied: Mg with Pb, Sn, Zn, Sb, Bi. In these cases a small but noticeable amount of the compound is found in the block obtained by alternately compressing and filing down again. In general the block is composed of fragments of the components surrounded by films of the compound.

III. The metals form one or more series of mix-crystals. Examples studied: the compound MgCd with Mg and Cd; Bi–Tl, Pb–Tl, Sn–Cu, Zn–Cu, Al–Mg. In such cases the condition of the compressed block varies with the lapse of time after compression. Diffusion, promoted by the intimate contact consequent upon the compression, sets in and proceeds at a rate characteristic of the particular system; this is usually extremely small at ordinary temperatures, but in some cases is noticeable in the course of a few days. As diffusion progresses the condition of the compressed block approaches gradually the equilibrium condition. The rate of diffusion increases very rapidly at higher temperatures;* so that by keeping a compressed block for a sufficient time at a temperature away below its lowest melting point, its structure becomes identical with that of the block obtained by fusion.

It is to be noted, however, that these effects are not the direct result of the compression, for a block immediately after compression is for practical purposes entirely a conglomerate of fragments of the two components. The sole effect of compression in these cases is to effect intimate and thorough contact between the two components; by so doing, it promotes diffusion, which is the primary cause of the changes observed. Moreover, it is almost certain that the same state of equilibrium would be reached by the action of diffusion, without previous compression of the system, provided that sufficient time is given—a condition easily fulfilled in geological work. In those cases in which the metals form both compounds and series of mix-crystals (as in some of the systems mentioned under III) the total effect is an aggregate of the effects summarized under II and III.

Hence, the general conclusion of the whole matter is, that compression alone does not result in the production of true

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* Thus, diffusion in the system Bi–Tl is more than 1000 times as great at 120° as at ordinary temperature.

alloys. In those systems in which the metals crystallize out from the melt as pure components, there is no essential difference between the conglomerate produced by compression and that obtained by fusion. In all other systems the immediate effect of compression is slight and consists solely in the fact that compression brings about very intimate contact between the particles, the result of which, in turn, is the formation at the contact of a compound (if such be possible) or the promotion of diffusion (when the metals can form mix-crystals).

THE WORK OF G. SPEZIA.

Spezia has performed a number of experiments on the effect of pressure on chemical reactions and transformations; and has reached conclusions in harmony with those presented in this paper.

In 1898 he noted that opal from Baldassero, treated for seven days at a temperature of 280–290° with a dilute solution of sodium silicate, was transformed into quartz. On the other hand a prism of the same opal immersed for eight years in the same solution at a temperature never above 30° and under a pressure of 1600 atmospheres, showed no evidence of such transformation.*

He has lately published an account† of similar work, undertaken chiefly to disprove certain assertions made by Van Hise‡ with regard to the effect of pressure in bringing about silicification, dehydration and deoxidation. These experiments are presented in summary form below.

TABLE VII.—Spezia's Experiments on the Influence of Compression on Certain Reactions at Ordinary Temperature.

	System	Compression		Result
		Amount in atm.	Duration	
I.	Hydrated silica + $CaCO_3$	6000	1 year	No trace of reaction
II.	Alum ($K_2Al_2(SO_4)_4.24H_2O$) + powdered quartz	8000	8 months	Absolutely no dehydration of the first named substances
	Alabaster + powdered quartz			
	Limonite + Powdered quartz			
III.	Göthite + quartz	9500	26 days	No dehydration
IV.	CuO (powder) + Mg (filings)	9500	30 days	No trace of reaction
	CuO (powder) + K	9500	30 days	No trace of reaction
V.	Calcite	7000	6 months	Absolutely no change
	Aragonite	7000	6 months	Absolutely no change

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* Rivista Min. Ital., xxxv, 62–64, 1908.

† Atti Accad. Sci. Torino, xlvi, 1, 1911.

‡ "Treatise on Metamorphism" (U. S. Geol. Survey, Monograph No. 47).

These results are in agreement with the geological evidence and with what one would expect from general principles; they required to be demonstrated practically only because statements to the opposite effect had been made and, apparently, accepted.

THE INTERDIFFUSION OF SOLIDS.

Closely related to the subjects discussed above is the question of the interdiffusion of solids. Various early isolated observations had been made,* but the first thorough investigation was made by Roberts-Austen,† on systems composed of two metals. Spring‡ also made some experiments along this line, and since that time a few isolated observations have been recorded, amongst them those already referred to on the system $BaCO_3 - Na_2SO_4$, and those of Masing on alloys.

The general conclusion from this work is that diffusion between solids is appreciable, but only in those systems in which solid solutions can form, as indeed one might expect *a priori;* and that the rate of diffusion increases enormously with rise of temperature. As regards the effect of uniform pressure on the rate of diffusion, some experiments made in this laboratory indicate that subjecting a system to uniform pressure is accompanied by an increased rate of diffusion; but it is premature to consider this as established, and it would be still more hazardous to generalize from this that uniform pressure should always have such an effect.

GENERAL REMARKS.

To some the hypothesis made use of in the foregoing discussion—namely, that every *permanent* deformation of a crystalline aggregate is conditioned by a real local melting—may appear to be of rather daring character, despite the fact that it has been shown to reconcile successfully some divergences hitherto outstanding. In reply to such persons, we would observe that the criterion by which a hypothesis is to be judged is not so much its inherent fitness to take a place in the group of our preconceived notions of the behavior of matter, as its usefulness in correlating known facts and in suggesting new inquiries. And it is precisely on this account that we deem the hypothesis here advocated to be satisfactory, since it does provide a definite basis for new experimental work; whereas the older hypotheses tend to be mere *post facto* descriptions of the phenomena, and to lead nowhither.

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* See Winkelmann's Handbuch der Physik, 2 Aufl., vol. i, 1505.

† Phil. Trans. Roy. Soc. London, clxxxvii, 383, 1896.

‡ Zs. physik. Chem., xv, 65–78, 1894; Bull. Acad. Roy. Belg. (3), xxviii, 23–46, 1894.

This hypothesis can be made use of only when the deformation is permanent; in other words, it is inapplicable (and unnecessary) so long as the material is within its elastic limit. It applies primarily to crystalline aggregates, but this statement does not imply that it accounts completely for the behavior of systems composed of a single crystal or of similar crystals similarly oriented—in short, of systems where the vectorial crystal forces are more or less dominant—when exposed to the action of external forces. Indeed, it in no wise precludes the use of other explanations to account, for instance, for the presence and occurrence of cleavage and gliding planes in crystals, which may well be a different phenomenon, associated or not with the phenomena discussed in the foregoing pages. Yet so far as the writers are aware, the explanation of gliding planes commonly advanced and accepted by crystallographers and geologists does not conflict with that which follows from the viewpoint of the present paper in any point which can be decided by direct experimental evidence at the present time.

It may be of service, in rendering the conception more concrete, to present a brief outline of a possible mode of action of unequal pressure on crystalline solids. We will suppose that the ultimate crystal particle is the real molecule of the substance; this molecule is in general, if we may say so, a polymer of the simplest chemical formula which expresses the relative composition of the substance, its mean degree of polymerization depending on the external conditions of temperature and pressure. In other words, dissociation of the complex increases with increasing temperature (and decreasing pressure), until at a certain point, so much of the new phase (still in general a polymer, though less complex than that stable at lower temperatures and higher pressures) is formed that a transformation occurs; this point is either a transition point or a melting point, according as the new phase is crystalline or fluid.*

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* Similarly, for transformations of the liquid phase into another phase, either liquid or gaseous, the gas phase is usually considered to be made up of molecules polymerized very slightly, if at all. The above viewpoint would seem to be quite generally accepted in the case of the substance water, at least, steam being supposed to be $(H_2O)_n$, liquid water $(H_2O)_{2n}$, and ice $(H_2O)_{3n}$ or $(HO)_{4n}$, n being a small integer; for this particular substance, indeed, it would be difficult to imagine a way of accounting for the maximum density, except by a hypothesis involving the presence in the liquid phase of more than one molecular species. Further evidence in favor of this viewpoint is afforded by facts such as the possibility of heating certain solids above the melting point, and the behavior of certain substances on melting, e. g., antimony if heated only slightly above its melting point, but still to all appearances completely melted, and then cooled, may crystallize just as if the original crystal framework had not been destroyed.

Now imagine our molecular complex exposed to uniform pressure: it would merely be compressed, and would regain its original state when freed from compression. Following out this conception, too, we should expect that uniform pressure would increase the stability of the complex; and this is what we find, since uniform pressure raises the melting point of practically all substances.

With unequal pressure, on the other hand, it is otherwise. For if, the temperature being kept constant, a gradually increasing one-sided pressure—that is, a shearing *stress*—be applied to the complex, it will ultimately overcome the resistance offered by the complex, causing a dissociation of the latter into one or more simpler molecular species; and if this molecular species is that characteristic of the liquid phase of the substance, we have a melting—or something exactly equivalent to it—which takes place at a perfectly definite pressure, the magnitude of which depends on the temperature. Now, if our particle is within a crystal—that is, if it is surrounded by a configuration of similar particles, arranged, as it would seem they must be if we are to account for compressibility, in such a way that there are spaces of some kind between the particles—the melted parts will flow away, thus relieving the stress, and quickly recombine to form the complex which is stable under the particular conditions; for no conditions could be imagined more favorable to recrystallization, especially if there be any reality corresponding to the idea that a particle exerts influence within the space surrounding it. According to this view, then, we need scarcely be surprised if the particle in recrystallizing regained its original orientation.

It may be urged that the general hypothesis is inapplicable in the case of substances—for instance, quartz—which form highly viscous melts or which dissociate on melting; but these objections lose weight if we remember (1) that viscosity of the melt will result only in an increase in the apparent melting pressure by an amount sufficient to overcome the viscosity; (2) that the condition of the melt as obtained under ordinary pressure is absolutely no criterion of its condition under high pressure; indeed, it appears to be a fact in harmony with the views outlined above that pressure tends to inhibit dissociation, or to favor recombination. Moreover, it is in no wise essential to the success of the hypothesis that the substance should in every case completely recrystallize; for, since the total fraction which melts during the deformation is in all probability very small indeed, it seems to us doubtful if even the most refined optical methods now in use are sensitive enough to enable us to detect with certainty the presence of the small quantity of sub-cooled liquid resulting from the process. Indeed there is evidence in the case of the metals which indicates that complete recrystallization does not occur; for the density of a piece of metal which has been deformed is always less than that of the same sample after annealing,* which is precisely what we should expect if the metal after deformation contains some small fraction in the form of subcooled liquid.

Summary and Conclusion.

In all discussions of the influence of compression on solid systems it is essential that we bear in mind the distinction between the effects of uniform pressure and of non-uniform pressure; disregard of this distinction is responsible for many of the apparently contradictory statements to be found in the literature pertaining to the subject.

Uniform pressure has a comparatively slight effect on the melting point: it usually raises it, and by an amount which, in the systems hitherto investigated, is seldom greater than 10°, and never greater than 30°, per 1000 atmospheres. Its effect on solubility is slight, and for practical purposes negligible as compared with the influence of temperature upon solubility. Uniform pressure tends to further those reactions which are accompanied by a decrease of volume; but it by no means follows that it will cause these (or other) reactions to occur; for whether a reaction takes place or not is determined primarily by its velocity under the particular conditions, and such evidence as there is tends to show that reaction velocity is not much affected by uniform pressure.

The effects of non-uniform pressure greatly outweigh those of uniform pressure. It *always* lowers the melting point and raises the solubility, and by amounts which are many times greater than the corresponding changes with uniform pressure. Indeed if we make the plausible assumption that *permanent* deformation of a crystalline aggregate is conditioned by a real local melting (of those parts, which at any moment bear the brunt of the load), we find the amount of pressure required to cause melting at ordinary temperature to be well within the bounds of probability. Such we believe to be the efficient cause in producing most of the phenomena recorded as occurring when solid systems were submitted to compression.

From a discussion of the results from this standpoint the following conclusions emerge:

(1) That the amount of compression required to cause crystalline solids to "flow" or to weld together is dependent mainly on the melting temperature, heat of melting and

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* See Johnston and Adams, J. Am. Chem. Soc., xxxiv, 563, 1912, or Zs. anorg. Chem., lxxvi, 274, 1912.

density of the substance, and on the temperature of experiment; consequently there is a rough parallelism between ease of flow and melting point, the substances with the highest melting points being those which at any fixed temperature require the greatest force to weld them.

(2) That compression will not in general cause crystallization of a material, or the transformation of one form into another; it will do so in certain cases, where the other conditions are such that the velocity of transformation is appreciable; and will cause a partial transformation wherever the conditions are such that a partial melting occurs.

(3) The conditions for the furtherance of chemical reactions by compression are similar. With uniform pressure the reaction takes place only at the surfaces of contact, and hence only a small total amount of compound is formed; but when the compression is not uniform, there is a renewal of the surfaces which allows the reaction to proceed farther. This renewal is the result of a direct abrasive action and may also be advanced by a melting, and flowing away, of the reaction product, if its melting pressure is attained. In other words, the effect of non-uniform compression is precisely the same as that of grinding together the reacting substances in a mortar.

(4) Several of the criteria used by Spring to determine the condition of compressed systems are altogether insufficient; for example, no statement whatever can at present be made as to the equilibrium in the *solid* state of the system

$$BaSO_4 + Na_2CO_3 \rightleftarrows Na_2SO_4 + BaCO_3$$

The only justifiable deduction possible from his work with this system is that, on adding water to a mixture composed of either of the above pairs of substances, the amount transformed in a given short time depends upon the thoroughness with which the mixing was performed—a conclusion by no means new.

(5) With regard to the formation of alloys, the conditions are the same as those affecting chemical reaction. Where solid solutions are possible—either between metals or other substances—the intimate contact produced by compression promotes diffusion; but it is altogether probable that the effect of compression in furthering the formation of solid solutions (and possibly in promoting diffusion) is limited to this subsidiary rôle.

In general then, the effectiveness of compression applied to solid systems depends (1) upon its character (uniform or otherwise), (2) upon certain physical constants of the material, notably its melting point, but also its latent heat of melting (the value of which is known at present for a very few substances only), and its density. The viscosity is of minor importance, since it affects only the rate with which the final condition is attained, but not the position of equilibrium. The viewpoint adopted in this paper serves to harmonize the outstanding discrepancies in the literature pertaining to the effect of high pressure on solids.

Under geological conditions, high uniform pressure is always accompanied by fairly high temperature, which is a very much more efficient agency in effecting changes than high uniform pressure is. The effect of unequal pressure is, as we have seen, many times as great as that of uniform pressure; nevertheless even with unequal pressure, the effect of change of temperature is so very important that the two factors must be considered simultaneously. Moreover, the extent to which a reaction proceeds (for example $MSiO_3 + CO_2 \rightleftarrows MCO_3 + SiO_2$ in presence of water*) depends upon the relative solubilities (or rather relative insolubilities), *under the particular conditions*, of the various substances concerned in the reaction. The effect of uniform pressure on solubility is usually insignificant; that of temperature, on the other hand, is commonly large and very different for different substances. Hence, temperature alone may easily cause the reversal of a reaction (as in the case above) and in this regard far outweighs in general the effect of unequal pressure; with uniform pressure alone such a reversal is unlikely.

Finally it is to be noted that we can determine the effects of compression on a solid system only if we can define the character of the compression (with reference to its approach to uniformity or otherwise) as well as its magnitude; and even then, only when the requisite thermal and other data, characteristic of the system, are available. But these data, when once they are available, should—at least if the viewpoint of the present paper proves to be satisfactory—provide a basis for attacking the very fundamental question of the limiting stress-difference at which flow sets in for any solid aggregate, and the variation of this limit with the temperature of the material, and hence, in the case of a rock mass, with its depth below the surface of the earth.

Geophysical Laboratory,
Carnegie Institution of Washington,
Washington, D. C., January, 1913.

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* If no solvent is present, the position of equilibrium depends upon the relative volatility of the various substances under the specified conditions. This statement is exactly analogous to that made in the text, if we remember that volatility may be regarded as solubility in a vacuum.

ART. XX.—*On the Coefficients and Exponent of the Radiation Equation, $K_{10} = cT_{10}^{a}$, in the Earth's Atmosphere*; by FRANK H. BIGELOW.

IN my paper on this subject, in this Journal for December, 1912, the values of the exponent A, in the equation,

$$\frac{K_1}{K_0} = \left(\frac{T_1}{T_0}\right)^A \qquad (1)$$

were computed from the observed temperatures T_1, T_0, on the top and bottom of a given stratum, through the radiation K_1, K_0. The values of A depend upon the ratio T_1/T_0, and wherever the temperature changes but slightly in passing through a stratum, for example 1000 meters thick, as occurs in the isothermal region, these are often very large. When T_1 is a little less than T_0, A is large and positive; when T_1 is a little larger than T_0, A is large and negative. The immediate problem is, therefore, to determine the coefficient and exponent in

$$K_{10} = c\, T_{10}^{a}, \qquad (2)$$

corresponding with the radiation equation. The ratio equation was formed on the supposition that for two levels $c_1 = c_0$, and $a_1 = a_0 = A$, as for instance,

$$\frac{K_1}{K_0} = \frac{c_1 T_1^{a_1}}{c_0 T_0^{a_0}} = \left(\frac{T_1}{T_0}\right)^A \qquad (3)$$

In the free air this is not usually the fact, so that the special case cannot be accepted as general, and the values of c_1 and c_0, or a_1 and a_0, are not equal to each other. We proceed as follows (Table 1, page 255):

In order that the terms of the problem may be more fully understood, the several steps are reproduced from the computations on the balloon ascension of May 5, 1909, at Lindenburg, Germany, in latitude 52°, and by applying the working formulas in succession to the observed temperatures at the several levels from 116 to 17,000 meters, we compute the following terms: n the ratio of the adiabatic to the observed temperature-fall in the several strata, P the pressure in kilograms per square meter, ρ the density of the air per cubic meter, R the variable gas coefficient in the Boyle-Gay Lussac Law, $P = \rho\ RT$,* Cp_{10} the mean non-adiabatic specific heat in the stratum, $\frac{1}{2}(q_1^2 - q_0^2)$ the change in the kinetic energy of circula-

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* The usual gas equation is assumed to be applicable, although heat transference to neighboring air masses and air circulation can not be prevented in the free air. Consequently. the non-adiabatic gas coefficient, R_{10}, must vary, while R_a obtained from laboratory experiments under adiabatic condi-

Table 1.—Example of the computation of a and log c from the observed temperature T. Lindenburg, May 5, 1909.

z Height	T Temp.	n Ratio	P Pressure	ρ Density	R Gas-coef.	Cp_{10} Spec. Heat	$\frac{1}{2}(q_1^2-q_0^2)$ Velocity	$\frac{P_0-P_1}{\rho_{10}}$ Gradient	Δ Check
17000	213·5	1·0966	9054	0·2253	188·24	652·90	− 3·6	6437·6	+ 6·2
16000	222·5	−5·4830	10590	0·2518	188·99	671·90	− 5·6	6629·2	+ 2·0
15000	220·7	−9·8694	12356	0·2810	199·21	707·01	−11·2	6963·7	+ 14·0
14000	219·7	−3·5248	14427	0·3138	209·28	746·08	− 9·2	7357·0	+ 6·3
13000	216·9	−1·7624	16871	0·3507	221·78	796·48	− 5·6	7851·0	+ 9·7
12000	211·3	5·8055	19790	0·3928	238·40	841·44	− 1·7	8300·4	+ 4·1
11000	213·0	1·1749	23248	0·4405	247·76	860·54	+ 0·9	8489·0	+ 4·0
10000	221·4	1·0846	27209	0·4926	249·44	864·93	− 0·9	8530·6	+ 5·7
9000	230·5	1·1215	31650	0·5485	250·29	868·38	− 8·1	8565·0	+ 5·4
8000	239·3	1·1749	36604	0·6083	251·44	872·99	−13·2	8615·8	+ 0·1
7000	247·7	1·2493	42120	0·6722	252·96	879·07	−16·1	8668·8	+ 7·0
6000	255·6	1·3520	48242	0·7403	254·95	886·91	− 8·8	8750·2	+ 3·0
5000	262·9	2·3498	55039	0·8130	257·48	900·93	− 5·2	8885·0	+ 6·6
4000	267·1	1·7016	62609	0·8910	263·05	917·48	− 5·4	9051·5	+ 3·5
3000	272·9	2·1455	71054	0·9750	267·05	928·87	− 7·0	4589·3	− 5·6
2500	275·2	3·0842	75630	1·0192	269·63	939·02	−11·7	4636·4	− 2·6
2000	276·8	3·5248	80462	1·0651	272·91	950·75	+ 5·9	4689·1	+ 2·5
1500	278·2	3·2898	85568	1·1127	276·41	962·72	+22·1	4738·9	+ 11·8
1000	279·7	−4·9347	90958	1·1621	279·83	979·01	+32·5	4813·8	+ 17·3
500	278·7	1·4576	96676	1·2136	285·82	991·48	+11·5	3753·8	+ 3·7
116	281·3	—	101309	1·2547	287·03	—	—	—	—

Lindenburg, May 5, 1909, continued.

z Height	Q_1-Q_0 Heat	S_1-S_0 Entropy	W_1-W_0 Work	U_1-U_0 Energy	K_{10} Radiation	A Exponent	log C Coeff.	log c Coeff.	a
17000	−3358·6	−15·406	4575·5	−7934·1	−16953	3·50	—	—	—
16000	−3169·2	−14·301	4639·9	−7809·1	−19066	−10·34	+28·034	−5·435	3·764
15000	−2817·1	−12·793	4944·7	−7761·8	−20737	−21·11	+52·871	−5·461	3·775
14000	−2433·5	−11·148	5227·2	−7660·7	−22820	− 5·78	+16·828	−5·489	3·787
13000	−1939·7	− 9·061	5578·6	−7518·3	−24578	− 3·41	+10·437	−5·537	3·810
12000	−1499·8	− 7·068	5900·8	−7400·6	−26872	13·29	−27·533	−5·563	3·822
11000	−1313·9	− 6·049	6035·7	−7349·6	−29889	4·40	− 6·181	−5·548	3·814
10000	−1268·8	− 5·614	6064·3	−7333·1	−35443	3·09	− 3·288	−5·558	3·819
9000	−1227·5	− 5·107	6086·8	−7314·3	−40838	3·62	− 4·021	−5·558	3·819
8000	−1176·9	− 4·833	6122·9	−7299 8	−46733	4·26	− 6·506	−5·560	3·820
7000	−1114·1	− 4 428	6157·8	−7271·9	−53117	3·95	− 5·249	−5·557	3·819
6000	−1044·0	− 4·028	6218·9	−7262·9	−60123	3·89	− 5·401	−5·560	3·820
5000	− 909·2	− 3·431	6314·8	−7224·0	−67075	6·48	−11·132	−5·547	3·814
4000	− 745·6	− 2·762	6434 0	−7179·6	−74322	3·63	− 4·050	−5·560	3·820
3000	− 312·3	− 1·140	3263·1	−3575·4	−80347	5·25	− 8·115	−5·567	3·823
2500	− 257·5	− ·933	3294·4	−3551·9	−83970	9·23	−18·387	−5·577	3·828
2000	− 217·3	− ·783	3335·5	−3552·8	−88378	9·81	−20·982	−5·590	3·833
1500	− 174·4	− ·625	3372·8	−3547·2	−92858	7·64	−14·180	−5·601	3·838
1000	− 104·4	− ·374	3427·5	−3531·9	−96765	− 8·29	+24·708	−5·593	3·834
500	− 19·5	− ·070	2671·6	−2691·1	−99671	—	—	—	—
116	—	—	—	—	—	—	—	—	—

The sign (—) of K_{10} indicates a decreasing radiation energy outward along the positive radius r.

tion, $\frac{P_0-P_1}{\rho_{10}}$ the mean pressure gradient per unit density, Δ the difference required to balance the check equation,

$$g(z_1-z_0) = -\frac{P_1-P_0}{\rho_{10}} - \tfrac{1}{2}(q^2_1-q_0^2)-(Q_1-Q_0), \qquad (4)$$

(Q_1-Q_0) the change in the heat of each cubic meter of air in passing from one level to the other, (S_1-S_0) the entropy change, (W_1-W_0) the work done in expanding the air, (U_1-U_0) the internal energy, K_{10} the mean radiation energy in the stratum, A the exponent in the ratio equation (1).

In order to separate the constituent coefficients c_1, c_0 and the constituent exponents a_1, a_0 we first compute the coefficients by using the exponent A, in

$$K_{10} = C\ T_{10}^{A} \qquad (5)$$
$$\log K_{10} = \log C + A \log T_{10}. \qquad (6)$$
$$\log C = \log K_{10} - A \log T_{10}. \qquad (7)$$

An example of this result is given in Table 1, under log C. In all cases the mean values T_{10} are taken to correspond with the mean values K_{10} for the stratum. It should be stated that in arranging Table 1 the values of T, P, ρ, R are given for the level of the elevation, as in the height column z, but that for all the derived values of n, Cp_{10}, and so on, the values against a given elevation are the means for the stratum of which this elevation is the top, and the lower one the bottom of the stratum. Since the computation of A, log C, depends upon two preceding steps, there are two vacancies in the column just below. One can supply these omissions by selecting shorter steps in the lower levels, 0, 200, 400 meters, as has been done in computing the diurnal convection. Comparing log C with the observed T it is seen that A is negative for $T_1 > T_0$, and that A and log C have opposite signs, so that the coefficient C is negative. The sign in log C applies only to the characteristic of the logarithm, so that, for example, $-14{\cdot}180 = 1{\cdot}52 \times 10^{-14}$. Similar computations have been made for twelve balloon ascensions, of which ten are mentioned in Table 4; the mean values T have been constructed for the hemisphere, in elevation from the surface to 19,000 meters for every 1000 meter level, and for every 10° in latitude from the equator to the north pole. Hence, we have two large series of the values of log C, (1) from twelve original balloon ascensions, and (2) from many mean

tions is a constant. Similarly, the so-called specific heat is a ratio, or coefficient, $Cp_a = dQ/dT = (Q_a - Q_0) \div (T_a - T_0)$, constant so long as only adiabatic expansion and contraction occur, but otherwise variable. The adiabatic specific heat Cp_a, which exists only in textbooks and laboratories, ceases to be applicable on entering the field of meteorology.

series of balloon soundings as extended to cover the hemisphere provisionally, and to represent the average summer conditions of the northern hemisphere.

On examining the relations between A and log C, it is to be noted that they increase and diminish together, apparently in a simple linear relation. Accordingly these values have been collected in two groups, and the means taken by sets, including the same integer of A.

TABLE 2.

The Mean and Adjusted Values of A and log C.

Lindenburg and the Tropics			Northern Hemisphere			Adjusted Values	
No.	A	log C	No.	A	log C	A	log C
10	2·749	− 2·900	..	...	...	3	− 3·740
47	3·562	− 4·797	21	3·740	− 5·402	4	− 5·960
60	4·420	− 7·115	41	4·515	− 7·138	5	− 8·180
25	5·418	− 8·953	53	5·486	− 9·274	6	−10·400
17	6·509	−11·738	9	6·307	−10·967	7	−12·620
5	7·464	−14·322	3	7·397	−13·548	8	−14·840
1	8·230	−16·689	..	...	...	9	−17·060
4	9·523	−19·584	..	...	...	10	−19·280

The first column under each group gives the number of observations, the second the value of the exponent A, and the third the value of log C as the mean.

Plotting these data on fig. 1, they fall generally on a straight line whose equation may be written,

$$\log C = \log C_0 + (A - 4) \log B, \tag{8}$$

$$C = C_0 B^{A-4}, \tag{9}$$

$$\log C = - 5{\cdot}960 - 2{\cdot}220\,(A - 4), \tag{10}$$

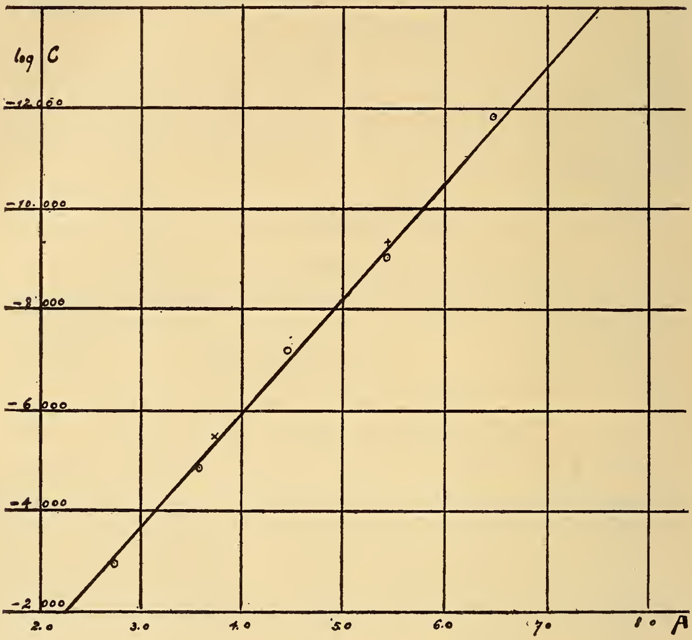
where $\log C_0 = - 5{\cdot}960$, $\log B = - 2{\cdot}220$.

The form of this equation is the same as that for the incoming radiation in the atmosphere

$$I = I_0\, p^m$$

and their relations may be examined.

FIG. 1.



In order to apply this function to the problem we can substitute in (5), noting now by log c and a those values of log C and A which form a pair, and satisfy the equation,

$$\log K_{10} = \log c + a \log T_{10} \tag{11}$$

$$\log K_{10} = -5{\cdot}960 - 2{\cdot}220\,(A - 4) + a \log T_{10} \tag{12}$$

It is found by trial that the values of a in the atmosphere lie between 3·50, the theoretical exponent for dry air, and 4·00, the exponent in the Stefan Law for a radiating black body, in which the Kurlbaum coefficient is $\sigma = 5{\cdot}32 \times (10)^{-4}$, in K.M.S. units and $\log \sigma = -4{\cdot}7259$. A working table for A and log C will facilitate the computations. (Table 3.)

In the equation for adjustment,

$$\log c = \log K_{10} - a \log T_{10},$$

we have T_{10} from direct observation and K_{10} from computations depending on T_1, T_0, and it is evidently necessary only to find the pair values (a, log c) by trial that will satisfy the given K_{10} and log T_{10}.

TABLE 3.

Evaluation of the equation,

$$\log C = -5{\cdot}960 - 2{\cdot}220\,(A-4)$$

between the limits A = 4·00 and 3·50.

A	log C	A	log C	A	log C	A	log C
4·00	−5·960	3·85	−5·627	3·70	−5·294	3·55	−4·961
3·99	−5·938	3·84	−5·605	3·69	−5·272	3·54	−4·939
3·98	−5·916	3·83	−5·583	3 68	−5·250	3·53	−4·917
3·97	−5·893	3·82	−5·560	3·67	−5·227	3·52	−4·894
3·96	−5·871	3·81	−5·538	3·66	−5·205	3·51	−4·872
3·95	−5·849	3·80	−5·516	3·65	−5·183	3·50	−4·850
3·94	−5·827	3·79	−5·494	3·64	−5·161	--	--
3·93	−5 805	3·78	−5·472	3·63	−5·139	--	--
3·92	−5·782	3·77	−5·449	3·62	−5·116	--	--
3·91	−5·760	3·76	−5·427	3·61	−5·094	--	--
3·90	−5·738	3·75	−5·405	3·60	−5·072	--	--
3·89	−5·716	3·74	−5·383	3·59	−5·050	--	--
3·88	−5·694	3·73	−5·361	3·58	−5·028	--	--
3·87	−5·671	3·72	−5·338	3·57	−5·005	--	--
3·86	−5·649	3·71	−5·316	3·56	−4·983	--	--

TABLE 4.—Observed Temperature T.

z Height in meters	May 5 1909 52°	July 27 1908 52°	Sept. 2 1909 52°	Sept. 7 1906 45°	Sept. 25 1907 35°	Sept. 9 1907 25°	Aug. 29 1907 13°	July 29 1907 13°	June 19 1907 −2°	Victoria Nyanza 0°
18000	—	223·2	—	—	—	—	—	—	—	190·5
17000	213·5	220·5	—	—	222·9	231·1	—	—	—	197·1
16000	222·5	219·9	—	225·9	220·2	227·3	—	—	—	202 6
15000	220·7	218·3	—	219·8	220·1	216·8	203 7*	205·1*	203·9*	206·8
14000	219·7	218·1	—	216·8	219·9*	213·4*	208·4	209·7	212·4	210·8
13000	216·9	216·5	226·3	215·0*	220 1	215·4	214·1	214·9	221·1	216·0
12000	211·3*	212·7*	228·1	223·9	220·3	220·4	220·8	221·8	225·8	222·6
11000	213·0	217·4	228·3	231·2	228·1	227·8	228·3	229·4	237·8	231·4
10000	221·4	225·9	228·0	241·4	236·0	238·0	237·3	237·4	245·8	238·9
9000	230·5	233·5	225·6*	249 4	246·0	246·5	245·9	246·7	253·6	246·1
8000	239·3	242·2	230 2	256·4	253·7	255·0	252·9	253·1	260·0	250·7
7000	247·7	250 6	237·8	262·7	261·1	262·1	258·9	262·1	266·5	258·0
6000	255·6	257·4	246·5	267·3	267·4	267·8	266·1	267·8	272·6	263·4
5000	262·9	263·5	250·7	274·9	274 0	274·9	272·5	272·4	276·9	269·2
4000	267·1	270·5	256·7	279·7	278·5	279·3	276.7	277·2	280·9	274.7
3000	272·9	275·7	264·1	287·3	281·9	287·1	282·2	283·0	286·5	280·8
2500	275·2	278·7	266·6	289·4	284·5	290·6	285·2	285·8	287·8	284·6
2000	276·8	282·5	268·9	293·7	287·1	293·4	289·4	283·9	290·2	288·4
1500	278·2	286·3	272·5	297·9	289·1	295·3	287·5	286·2	290·5	292·4
1000	279·7	290·0	275·5	301·2	290·5	297·8	291·1	290·1	292·7	296·2
500	278·7	290·4	278·1	301·7	293·5	297·4	295·9	292·7	296·2	(1140)
116	281·3	293·3	283·2	304·7	296·5	303·5	299·1	298·1	300·2	—

* Bottom of the isothermal region.

TABLE 5.—Computed Mean Radiation K_{10}.

z										
18000	—	−14844	—	—	—	—	—	—	—	−12005
17000	−16953	−16455	—	—	−17164	−17812	—	—	—	−13968
16000	−19066	−18108	—	−18316	−18937	−18356	—	—	—	−15993
15000	−20737	−19830	—	−19682	−20534	−19343	−18494*	−19084*	−19187*	−18060
14000	−22820	−21723	—	−21008	−22684*	−21006*	−20828	−20960	−22247	−20582
13000	−24578	−23633	−25775	−23673*	−25198	−23848	−24385	−24861	−25361	−23624
12000	−26872*	−26065*	−28216	−28146	−28705	−27952	−27661	−27729	−29381	−27013
11000	−29889	−29982	−29601	−32114	−32828	−31926	−31687	−32573	−33927	−31143
10000	−35443	−34455	−32418	−36303	−37127	−36541	−36668	−37471	−38635	−35422
9000	−40838	−39393	−39874*	−41651	−45250	−41644	−41899	−42075	−43824	−39717
8000	−46733	−45063	−43754	−46979	−48603	−46870	−46897	−47647	−49092	−44616
7000	−53117	−50795	−48907	−52993	−54642	−53287	−53578	−53601	−54567	−50082
6000	−60123	−57663	−54983	−57986	−60937	−59421	−57645	−59329	−60580	−55577
5000	−67075	−64159	−62070	−64247	−67550	−65154	−65311	−65799	−66084	−61930
4000	−74322	−71393	−68557	−71497	−73900	−72795	−71878	−72275	−70670	−68663
3000	−80347	−77044	−74030	−76570	−78842	−78592	−77492	−79073	−79033	−74258
2500	−83970	−81465	−78363	−82232	−83246	−82910	−81306	−81720	−82558	−78404
2000	−88378	−85810	−83759	−85756	−87206	−86782	−85834	−84500	−85954	−82802
1500	−92858	−90814	−87826	−90796	−91232	−90750	−88386	−89108	−89242	−87422
1000	−96765	−95018	−92312	−95183	−95408	−93306	−93764	−92385	−93418	—
500	−99671	−98622	−98345	−98222	−100065	−99682	−98933	−91412	−98622	—
116	—	—	—	—	—	—	—	—	—	—

Table 4 contains the observed temperatures T, from which the pair mean values T_{10} can be computed. Table 5 gives the corresponding values of the radiation energy K_{10}, being the mean for the stratum below its line of elevation z. The following examples from the balloon ascension of May 5, 1909, will illustrate the method of computing:

TABLE 6.

Computation of $\log c = \log K_{10} - a \log T_{10}$.

z	1000	1500	2000	2500	
T_{10}	279·2	279·0	277·5	276·0	
$\log T_{10}$	2·446	2·446	2·443	2·441	
Trial a	3·84	3·83	3·83	3·83	By Crelle's Tables.
$a \log T_{10}$	9·393	9·368	9·357	9·349	
K_{10}	96765	92858	88378	83970	
$\log K_{10}$	4·986	4·968	4·946	4·924	
$\log c$	−5·593	−5·600	−5·589	−5·575	
a	3·834	3·838	3·833	3·827	Adjusted.

This preliminary research has been conducted in three-place logarithms, and the multiplications $a \log T_{10}$ were made by Crelle's Tables. When the observational data of the balloon ascensions are sufficiently exact, it will be proper to compute these data somewhat more fully. In a similar manner Table 7 contains the values of $\log c$, and Table 8 those of a, throughout the ten selected balloon ascensions. An inspection of these tables shows that a generally decreases in value from 3·81 on the surface in the tropics to 3·79 on entering the isothermal layer, when it changes quite steadily to about 3·76 at 16,000 meters; the values of a increase from 3·81 to 3·83 in latitude at the surface. In fact there are no fixed values of a and log c in the atmosphere, though the range is not large. In order to exhibit the general distribution of these quantities Table 9 contains approximate values of a for every 10 degrees in latitude, and for every 1000 meters elevation computed from the provisional mean summer temperatures of the northern hemisphere.

TABLE 7.—The coefficient log c in $\log c = \log K_{10} - a \log T_{10}$.

z	May 5 1909 52°	July 27 1908 52°	Sept. 2 1909 52°	Sept. 7 1906 45°	Sept. 25 1907 35°	Sept. 9 1907 25°	Aug. 29 1907 13°	July 29 1907 13°	June 19 1906 −2°	Victoria Nyanza 0°
16000	−5·435	−5·433	—	−5·440	−5·445	−5·441	−5·492	−5·496	—	−5·456
15000	−5·461	−5·458	—	−5·449	−5·457	−5·470	−5·496	−5·499	−5·499	−5·476
14000	−5·489	−5·479	—	−5·474	−5·479	−5·487	−5·494	−5·501	−5·495	−5·467
13000	−5·537	−5·506	−5·481	−5·500	−5·521	−5·492	−5·506	−5·528	−5·498	−5·487
12000	−5·563	−5·529	−5·490	−5·515	−5·525	−5·516	−5·507	−5·500	−5·504	−5·486
11000	−5·548	−5·541	−5·510	−5·512	−5·528	−5·509	−5·507	−5·515	−5·498	−5·500
10000	−5·558	−5·540	−5·537	−5·502	−5·518	−5·503	−5·509	−5·516	−5·491	−5·502
9000	−5·558	−5·551	−5·571	−5·489	−5·516	−5·500	−5·513	−5·504	−5·509	−5·507
8000	−5·560	−5·542	−5·566	−5·499	−5·526	−5·503	−5·521	−5·519	−5·493	−5·514
7000	−5·557	−5·544	−5·558	−5 517	−5·534	−5·517	−5·536	−5·520	−5·500	−5·497
6000	−5·560	−5·535	−5·563	−5·518	−5·541	−5·526	−5·527	−5·509	−5·514	−5·511
5000	−5·547	−5·537	−5·585	−5·525	−5·530	−5·532	−5·524	−5·526	−5·527	−5·519
4000	−5·560	−5·548	−5·584	−5·534	−5·540	−5·544	−5·538	−5·527	−5·515	−5·529
3000	−5·567	−5·555	−5·585	−5·536	−5·554	−5·519	−5·543	−5·548	−5·538	−5·541
2500	−5·575	−5·560	−5·596	−5·548	−5·562	−5·526	−5·544	−5·534	−5·540	−5·527
2000	−5·589	−5·560	−5·606	−5·518	−5·544	−5·531	−5·537	−5·549	−5·550	−5·531
1500	−5·600	−5·561	−5·608	−5·523	−5·555	−5·539	−5·546	−5·553	−5·559	−5·532
1000	−5·593	−5·576	−5·561	−5·534	−5·563	−5·544	−5·546	−5·551	−5·563	−5·533

TABLE 8.—The exponent a in $K_{10} = c\,T_{10}^{a}$.

16000	3·762	3·760	—	3·763	3·766	3·764	3·787	3·789	—	3·771
15000	3·773	3·772	—	3·768	3·772	3·777	3·789	3·790	3·790	3·780
14000	3·786	3·781	—	3·779	3·782	3·785	3·788	3·792	3·789	3·776
13000	3·808	3·793	3·782	3·791	3·800	3·787	3·794	3·803	3·790	3·785
12000	3·820	3·804	3·786	3·798	3·802	3·798	3·794	3·791	3·793	3·784
11000	3·813	3·810	3·795	3·796	3·804	3·795	3·794	3·798	3·790	3·791
10000	3·817	3·809	3·808	3·792	3·799	3·792	3·795	3·798	3·787	3·792
9000	3·817	3·814	3·823	3·786	3·798	3·791	3·797	3·793	3·795	3·794
8000	3·818	3·810	3·821	3·791	3·803	3·792	3·800	3·800	3·788	3·797
7000	3·817	3·811	3·817	3·799	3·806	3·799	3·807	3·800	3·791	3·790
6000	3·818	3·807	3·820	3·799	3·810	3·803	3·803	3·795	3·797	3·796
5000	3·812	3·808	3·830	3·802	3·804	3·805	3·802	3·803	3·803	3·800
4000	3·818	3·813	3·829	3·806	3·809	3·811	3·808	3·803	3·798	3·804
3000	3·821	3·816	3·830	3·807	3·815	3·800	3·810	3·813	3·808	3·810
2500	3·827	3·818	3·834	3·813	3·819	3·803	3·811	3·806	3·809	3·803
2000	3·833	3·818	3·839	3·799	3·811	3·805	3·808	3·813	3·814	3·805
1500	3·838	3·818	3·840	3·801	3·816	3·809	3·812	3·815	3·818	3·805
1000	3·834	3·826	3·837	3·806	3·820	3·811	3·812	3·814	3·820	3·806

TABLE 9.—Approximate values of a for summer temperatures.

z	90°	80°	70°	60°	50°	40°	30°	20°	10°	0°
19000	*3.76*	*3·75*	*3·75*	*3·75*	*3·75*	*3·75*	*3·75*	*3·75*	*3·75*	*3·75*
18000	*3·77*	*3·76*	*3·76*	*3·76*	*3·76*	*3·76*	*3·76*	*3·76*	*3·76*	*3·76*
17000	*3·78*	*3·78*	*3·77*	*3·77*	*3·77*	*3·77*	*3·77*	*3·77*	*3·77*	*3·77*
16000	*3·79*	*3·79*	*3·78*	*3·78*	*3·78*	*3·78*	*3·78*	*3·78*	*3·78*	3·78
15000	*3·80*	*3·80*	*3·80*	*3·79*	*3·79*	*3·79*	*3·79*	*3·79*	3·78	3·79
14000	*3·81*	*3·81*	*3·81*	*3·80*	*3·80*	*3·80*	*3·79*	3·79	3·79	3·79
13000	*3·82*	*3·82*	*3·82*	*3·81*	*3·81*	*3·80*	3·80	3·79	3·79	3·79
12000	*3·83*	*3·83*	*3·82*	*3·82*	*3·82*	3·81	3·80	3·80	3·80	3·80
11000	*3·83*	*3·83*	*3·83*	*3·83*	3·82	3·81	3·80	3·80	3·80	3·80
10000	3·84	3·84	3·83	3·83	3·82	3·81	3·80	3·80	3·80	3·80
9000	3·84	3·84	3·84	3·83	3·83	3·82	3·81	3·80	3·80	3·80
8000	3·84	3·84	3·84	3·83	3·83	3·82	3·81	3·80	3·80	3·80
7000	3·85	3·84	3·84	3·83	3·83	3·82	3·81	3·80	3·80	3·80
6000	3·85	3·85	3·84	3·83	3·83	3·82	3·81	3·80	3·80	3·80
5000	3·85	3·85	3·84	3·83	3·83	3·82	3·81	3·81	3·81	3·81
4000	3·85	3·85	3·85	3·84	3·33	3·82	3·81	3·81	3·81	3·81
3000	3·86	3·86	3·85	3·84	3·83	3·83	3·82	3·81	3·81	3·81
2000	3·86	3·86	3·85	3·84	3·84	3·83	3·82	3·82	3·82	3·82
1000	—	—	—	—	—	—	—	—	—	—
000	—	—	—	—	—	—	—	—	—	—

The corresponding values of log c can be taken from Table 3. The italic types indicate the position of the isothermal region, and in it the values of a fall to about 3·75 at 19,000 meters whatever the value may be at a given latitude on entering this peculiar stratum or whatever its value at the surface. The rise in value from the equator to the pole is evident in all levels below the isothermal region. These then are the fundamental conditions to be considered in seeking a physical explanation of the isothermal region. It may be remarked in passing that these data afford no support for Abbot's hypothetical effective radiation layer, depending upon the heating effect of the aqueous vapor at about 4000 to 5000 meters elevation. Humphreys in several papers has given some general arguments in favor of the following hypothesis. Assume in the isothermal layer, and in the lower effective radiating layer,

Isothermal layer, ... $K_1 = b\,K_0 = c_1\,T_1^{a_1}$,

Lower effective layer... $K_0 = c_0\,T_0^{a_0}$,

whence, we have, ...

$$T_1 = \left(b\,\frac{c_0}{c_1}\right)^{\frac{1}{a_1}} T_0^{\frac{a_0}{a_1}}. \quad (14)$$

By a process of general reasoning Humphreys assumes that $K_1/K_0 = b = \frac{1}{2}$, and this can now be readily tested. Take the data from Table 9 for a, and thence log c by Table 3, for the latitudes 90°, 50°, 0°, and extract the respective values for the surface and at the bottom of the isothermal layer, and we have

Latitude	a_0	a_1	log c_0	log c_1	c_0	c_1	$\frac{a_0}{a_1}$	$\frac{c_0}{c_1}$
90°	3·86	3·83	−5·649	−5 583	$4·46 \times 10^{-5}$	$3·83 \times 10^{-5}$	1·01	1·16
50°	3·84	3·82	−5·605	−5·560	$4·03 \times 10^{-5}$	$3·63 \times 10^{-5}$	1·01	1·11
0°	3·82	3·78	−5·560	−5·472	$3·63 \times 10^{-5}$	$2·97 \times 10^{-5}$	1·01	1·22

$$\text{Hence,} \qquad T_1 = 0·87\ T_0, \qquad T_0 = 1·15\ T_1.$$

Check the formula against the data of Table 4.

Ascension	1	2	3	4	5	6	7	8	9	10
T_1	211°	213°	226°	215°	220°	213°	204°	205°	204°	—
T_0	242	245	260	247	253	245	235	236	235	—
z for T_0	7·5	7·8	3·5	9·3	8·0	9·2	10·2	10·2	11·3	—

There is no evidence that the assumed effective radiation strata are located at these elevations, z in kilometers. But assume that the effective radiations are those given in Table 5, and then the values of $1/b$, the ratio of K_0 at the surface to K_1 at the isothermal level, are

Ascension	1	2	3	4	5	6	7	8	9	10
$1/b = K_0/K_1$ ..	3·70	3·78	2·47	4·14	4·43	4·72	5·35	5 21	5·14	—

Means	3·52 at 50°	4·58 at 30°	5·23 at 10°
	$T_0 = 1·35\ T_1$	$T_0 = 1·41\ T_1$	$T_0 = 1·47\ T_1$

T_0 (computed)	285°	288°	305°	290°	310°	300°	300°	301°	300°	—
T_0 (observed) .	281	293	283	305	297	304	299	298	300	—

The value of K_1/K_0 is a wide variable, 3·5 to 5·2 at least, and Humphreys' arguments for $1/b = 2$ are not valid. There is no evidence that the planetary radiation described in his paper can be verified. It can be shown that his theorem of the relation between the "thickness of the water layer that would result from a condensation of the water vapor in the atmosphere *above any given* level . . . . may be expressed approximately by $d = 2w$," is not generally true.

Having derived values of log c and a for different conditions in the atmosphere, as represented by, (1) twelve balloon ascensions; (2) the northern hemisphere generally; (3) cyclones and anti-cyclones; (4) the diurnal convection at Cordoba, which will be published in Bulletin No. 3, Oficina Meteorologica Argentina, we can often avoid the long computation of the full series of formulas by computing K_{10} approximately from T_{10}, by (11).

Table 10.

$$\text{Log}\,(K_{10}) = \log c + a \log T_{10}$$

z	log K_{10}	log (K_{10})	Δ log (K_{10})	a	log c	log $(K_{10})_0$
6000	4·779	4·780	−0·001	3·820	−5·560	4·781
5000	4·827	4·789	+0·038	3·822	−5·564	4·826
4000	4·871	4·848	+0·023	3·825	−5·571	4·869
3000	4·905	4·886	+0·019	3·827	−5·575	4·906
2500	4·924	4·921	+0·003	3·828	−5·578	4·923
2000	4·946	4·955	−0·009	3·831	−5·585	4·946
1500	4·968	4·987	−0·019	3·834	−5·592	4·970
1000	4·986	4·971	+0·015	3·837	−5·598	4·984

From the data in the last two columns of Table 1, log c and a, compute log (K_{10}) in column 3, Table 10, and compare with log K_{10} in the second column derived from Table 1, as computed through the entire series of formulas. The differences Δ log (K_{10}) may be compensated by changing the value of a in Table 1 at the following rate, for $\Delta \log (K_{10}) = +0·0005$ we have $\Delta a = +0·001$. Correcting a of Table 1, as in column 5, Table 10, and taking the corresponding log c from Table 3, we find by formula (11) the log $(K_{10})_0$ thus adjusted in the last column, which conforms with log K_{10} in the second column. The required changes in a are a few units in the third decimal, and thus the entire series of formulas is checked.

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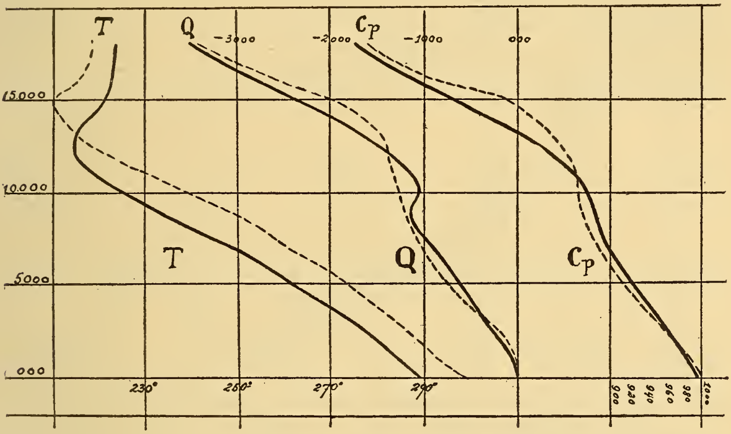
[*] Mt. Weather Bulletin, vol. 4, part 3, x, xi, xii.

From equation (4) we obtain the differential and fundamental equation connecting pressure, circulation and radiation,

$$-dP = g\rho dz + \rho q dq + \rho dQ$$
$$-dP = g dm + \rho q dq + \rho dQ$$

When there is no circulation and no radiation the variation of pressure is proportional to the change of mass, and this is the adiabatic state. This is the assumption which E. Gold makes in his paper,* but it excludes the radiation term under discussion from the several following dependent formulas. It is desirable to separate the various sources of radiation from the total effect in any layer, but it must be done through a direct study of the observational data in order to be able to construct a system of analytic equations that will classify the series of causes and effects. It is believed that the data in hand have such possioilities and the problems involved will be further studied.

FIG. 2. Temperature, Heat and Specific Heat.



Figs. 2 and 3 indicate some of the general reactions from the surface to 18,000 meters in height. The isothermal region begins generally in Europe at 12,000 m., but in the tropics at 15,000 m. The specific heat and the heat lost in the stratum have very similar distributions. The heat $(Q_1 - Q_0)$ has two sources of supply in addition to that of the radiating surface, as shown by the curves, the first in the lower cloud region of condensing aqueous vapor, 000 to 2,000 m., and the second at the upper

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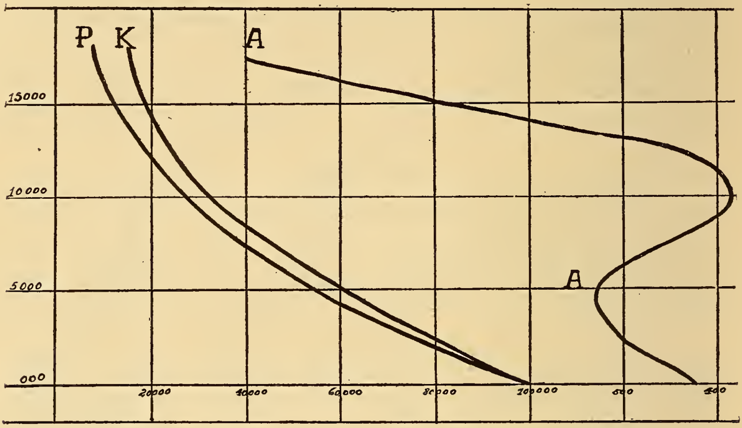
[*] The Isothermal Layer of the Atmosphere and Atmospheric Radiation, Proc. Royal Soc., A., vol. lxxxii, page 58, Reprint, 1908.

cloud region where the ice crystals ascending in the vertical convectional currents accumulate in layers just below the isothermal region, and intercept and store up some of the outflowing heat from the lower levels as well as incoming solar radiation. The fall of $Q_1 - Q_0$ is faster in the isothermal region than in the strata below it. The courses of the pressure P and the radiating energy K diverge slowly with the height, but the function connecting them can evidently be worked out, so that the computation between them may be shortened. The value of A has a maximum value 5·30 at 5,000 meters, a minimum at 10,000 of 3·82 which corresponds with the normal temperature gradient for radiation in the free air, with one end on the surface and the other in the isothermal region. As these values of A depend upon the temperature gradients and so upon the ratio T_1/T_0, it follows that the change of T_1 from its normal value for $A = a = 3·82$ must be due to special supplies of heat locally applied, as from the surface and the lower aqueous vapor, or from the heat stored up by congestion in the isothermal region. The relation of A to *a* at any level, therefore, becomes a means for studying the local as distinguished from the planetary radiation. The heat of the isothermal level is apparently due to a combination of the processes of hydrostatic pressure, circulation and physical rate of radiation through cold strata, 207° to 210°, to balance the total dynamic inward force of the earth's gravitation.

Fig. 3. Pressure, Radiation and Exponent A.



Entropy S, work W, and inner energy U are similar to Q; log C is similar to A. Continuous lines are for Europe and broken lines are for the Tropics.

Oficina Meteorologica Argentina,
Cordoba, Argentina, S. A., March, 1912.

Art. XXI.—*On a Simple Screw Micrometer*; by C. Barus.

In my last paper* I referred to a simple type of micrometer for interferometer work, consisting only of a screw with a light adjustable mirror at its end. Results with the screw were at first only moderately successful, so long as a single socket was used. But by replacing the single support by two supports *a* and *b* (fig. 1), slotting each parallel to the axis of the screw *SS* (as shown at *ss*) not quite through, so that the set screws on one side (elastic connection on the other) gave the play the necessary ease of motion to the exclusion of all wobble, the results were very much improved. Success was eventually reached by making the lugs or socket *ab* of indurated fiber instead of metal, and using a carefully cut brass screw. Fig. 1 shows the screw *SS* mounted on three leveling screws in

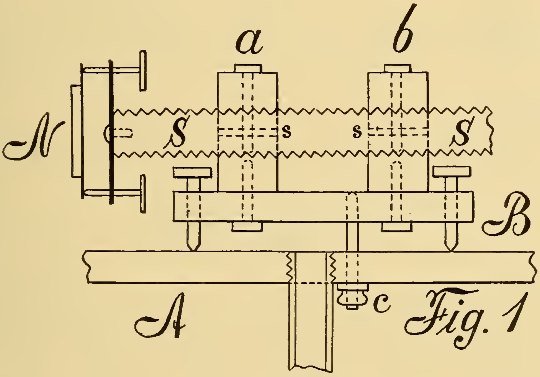


Fig. 1

B and locked at *c* to the table *A*. *N* is the mirror attachment, screwed to the end of *SS*.

Screws so cut (each nut one-quarter to one-half inch thick) are usually too tight at first, but they cling admirably. The necessary ease of motion was secured by the set screws at *a* and *b* (fig. 1), which here slightly push the socket apart. The ease with which a brass screw ten inches long and a pair of sockets of the kind in question may be cut and mounted, and their admirable precision of motion when tested by the interferometer, is astonishing.

Fig. 2 shows a comparison of the new screw No. 5 with the Fraunhofer micrometer, using about three inches of the former. The adjustment of the mirror of the latter (No. 5) was left incomplete, so that the directly reflected ray described a small circle in the telescope. The coincidence of images of the two interferometer mirrors *M* and *N* was secured at the beginning of each of the turns, by the initial adjustment, so that the ellipses

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* This Journal, xxxiv, p. 333–7, 1912.

reappeared with each complete turn, after the Fraunhofer micrometer had also been correspondingly displaced. Owing to the length (three inches) of the new screw used, it was necessary to use the Fraunhofer screw four times in succession, by introducing thick glass compensators into the ray coming from the new screw. These were made with thick plates of glass and added at the places indicated by *a*, *a'*, *a''*, in the figure. The total thicknesses of the piles of plates were

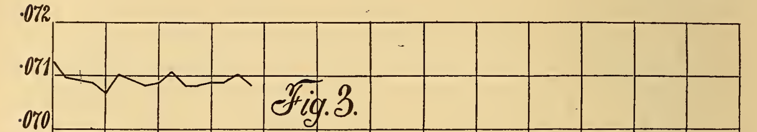
Fig. 3.

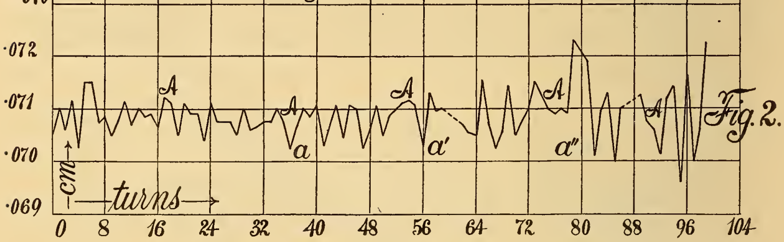
Fig. 2.

at *a*, 2·10 cm., 3 plates.
a' 5·60 cm., 8 plates.
a'' 8·60 cm., 12 plates.

Owing to the number of reflections (24 faces in the last case), the image gradually became more colored and less intense, so that the adjustment was gradually less certain. At the same time the shift of ellipses was less sensitive. It was, however, wholly the dimness of the interferences which made the adjustment more difficult, a result which could have been avoided by using a single plate of thick glass (about 9 centimeters); but this was not at hand. Finally a few adjustments of the Fraunhofer mirror were made for incidental reasons not connected with the precision of motion of the screw (as shown at *A* in figure). In other words, through the three inches of screw used no effect of flexure or other serious discrepancy could be detected, the ellipses returning in full strength after each complete turn.

The fluctuation of the curve which represents the equivalent of 1/36 inch in centimeters (*i.e.* here ·0705 centimeter), is largely within ·0005 centimeter at the beginning of the work, when seeing was good. This is about one division of the drum of the micrometer screw, or about 1/141 of the pitch of the screw No. 5 and is largely referable to the difficulty of setting the head of the new screw at zero, the disc and graduation having been improvised. It furthermore contains all errors of the Fraunhofer screw, and finally all errors in judgment in bringing the centers of ellipses back to the sodium line. Nevertheless, throughout the whole length examined the new screw retains a satisfactory mean pitch. The operation of comparison can easily be completed in one afternoon.

A similar screw with the two lugs but 1/4 inch thick and about 3 1/2 inches apart was now tested. The mirror mechanism was made lighter and the adjustment screws finer (56 threads to the inch), the object being to quite eliminate, if possible, the circular motion of the reflected ray. This is not easily accomplished, owing perhaps to an insufficiently plane mirror; but on rotating the screw in successive arcs of 90° the ellipses were usually available in three of the positions, though they were too blurred in the fourth for use; eventually they were visible throughout. For final adjustment besides a more perfect mirror (which need be only 1/2 inch in diameter) finer adjustment screws than the above would be desirable. The new comparison as a whole is given in fig. 3, in the same way as above. The fluctuation is on the average within about ·0003 centimeter, or half a scale part of the drum of the Fraunhofer micrometer and 1/236 of the circumference of the drum of the new screw. This uncertainty is wholly due to the difficulty of setting the latter with this precision, as the head was improvised in the laboratory for the purposes here in view.

To summarize: There seems to be no doubt, therefore, that a screw, satisfying the requirements of the interferometer and trustworthy to about ·0001 centimeter and a length of even a foot or more, could be constructed by the above method. It is necessary to begin with a straight rod for this purpose (or preferably with a tube) of a larger diameter, say 1 or 2 centimeters. The adjustable mirror at the end should be light, which was not the case in the above apparatus, ordinary thick plate glass 1 1/2 inch square being used. The adjustment screw with orthogonal axes must be of very fine pitch, if the image is to be stationary. Such a screw of low pitch, carefully cut in brass and running in sockets of indurated fiber, can be made in almost any laboratory.

The final advantage of this type of micrometer is the fact that the normal to the mirror is necessarily a prolongation of the axis of the screw and also coincides very nearly with the incident and reflected ray. There are thus no unknown angles between screw axis and normal to the mirror and exchange of screws at *M* and *N* is no longer necessary. When a mere comparison of screws is in question, it is sufficient to reduce the play of image in the telescope to a small circle, and this may be done in a few minutes.

Brown University, Providence, R. I.

Art. XXII.—*Pseudomorphs of Limonite after Marcasite;*
by H. B. North.

Pseudomorphs after pyrite and marcasite are frequently seen and those after the former mineral retaining perfect crystalline form are quite common. On the other hand, good pseudomorphs after marcasite are seldom seen, the usual museum specimen being scarcely more than a shapeless mass of limonite, showing no definite form of the mineral before alteration. In consideration of this it may be of interest to scientists in general and to mineralogists in particular to learn that a new find of limonite after marcasite has been made and that the specimens still retain the crystalline form of marcasite.

The new find was made in Richland County, Wisconsin, across the Wisconsin river from and directly north of the lead and zinc region. The mineral has been located on several hill tops, all within a radius of a mile. Many of the specimens were plainly visible on the surface of the ground or embedded in the grass, while others were found beneath the surface to a depth of 12 to 14 inches, in a sort of clay which is underlaid by sand. The best specimens, obtained just beneath the sod, have a dark red-brown color, a smooth hard surface and a good luster. The various faces are not in the least distorted and the edges are in perfect condition.

The specimens found on the surface of the ground are somewhat less brilliant in color, though in general they exhibit a perfect crystalline form. On the other hand, many of the crystals obtained from the layer of clay do not show a smooth surface but appear to have been etched to a slight extent. These specimens do, however, show perfect crystalline form. On one particular hill top on which the soil was very sandy, all specimens found have a yellowish brown coating. Several unusually fine specimens were found in this locality and many of the crystals exhibit faces not found on the specimens from the nearby hills.

The accompanying illustrations have been made from photographs of several of the better specimens. Fig. 1 (two-thirds natural size) shows the finest, though not the largest specimen found, the individual crystals being slightly larger than those on any of the other specimens. This specimen is 14·5^{cm} long and stands 7·5^{cm} high. It exhibits a parallel growth of 10 large crystals, the largest of which is 4^{cm} wide and 4^{cm} high. The specimen weighs 715 gms. The specimen shown in fig. 2 (two-thirds natural size) consists of a single and remarkably fine crystal surrounded at the base by several small crystals. The color of this specimen is a rich red-brown and the surface

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Figs. 1–3, two-thirds nat. size. Fig. 4, nat. size.

is unusually smooth and hard. The crystal is 2·8^{cm} wide and 4^{cm} high. The general shape of this crystal, as well as those shown in fig. 1, is of the Folkestone type (fig. 5, Dana's System of Mineralogy), though the indentations indicating twinning are not frequent. Several loose crystals of this general form were found, one of which is shown in fig. 3. Fig. 4 (nat. size) shows another well-defined though smaller crystal from the locality which yielded the yellow-coated specimens. This crystal, as will be seen at a glance, is of the Freiberg type (fig 6, Dana's System of Mineralogy), the face *c* being prominent. Many of the crystals from this particular locality show this same form.

A few specimens of limonite after pyrite were picked up in the same localities which yielded the pseudomorphs after marcasite. Upon another hill, at least two miles distant, a considerable deposit of limonite after pyrite was located, and upon this hill no specimens after marcasite were found. None of the specimens after pyrite are in the form of pyritohedrons or plain cubes, but all are cubes modified by octahedrons.

Specimens of this new find of limonite after marcasite can be seen at the National Museum in Washington, the American Museum of Natural History in New York, and in the mineral collections of Princeton University, Rutgers College, and the Case School of Applied Science. In addition, many specimens, including those shown in the accompanying illustrations, can be seen in the author's private collection at New Bruns wick.

Rutgers College,
New Brunswick, N. J.

Art. XXIII.—*The Floating Islands of Halemaumau;* by Frank A. Perret.

The view of the crater of Halemaumau—impressive always in its suggestion of potential, if not manifested, power—acquires, at times, a quality of extreme picturesqueness from the presence of an island, floating tranquilly and apparently unharmed, on the seething bosom of the glowing lava lake. And especially is this the case when, in the course of time and by agencies herein to be described, the rugged mass of rock is softened in its contours and embellished by a graceful line of shore; whilst a fitfully smoking summit lends a pleasing touch of harmony with an environment so eminently, and so essentially, volcanic. Such were the conditions—portrayed in fig. 1—which prevailed during the first weeks of the writer's investigation of Kilauea in the summer of 1911.

A study of the phenomenon will concern itself with the origin and formation of the islands, their flotation, growth, and the various vicissitudes incident to a more or less ephemeral existence amid surroundings of the most fervently destructive character.

The formation of these islands may occur in various ways. It not infrequently happens that, amid the swirling eddies of the surface lava, a certain area—balanced between opposing forces—remains, for a considerable time, at rest. There results the formation of a crust which gradually thickens by accretion from below and may also be built up by overflow movements of the surface material or by the spatterings from some neighboring fountain, until a true island is formed which may move about upon the lake under the influence of a changing surface current. Such islands are not, as a rule, of great mass and are rarely conspicuous while, being composed of comparatively easily fusible materials, their existence is generally a very brief one.

The formation of a central cone has, at times, been observed at Halemaumau. In 1891 such a cone attained a height of 200 feet* and these may be floated upon a rising lava column and be built up through internal ducts. Brigham believes some of the floating islands of Halemaumau to be "incipient central cones,"† and there can be no doubt as to this constituting one of the many processes by which, in this natural amphitheater where the powers of formation and destruction wage

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* Wm. T. Brigham: "The Volcanoes of Kilauea and Mauna Loa," p. 176. Memoirs of the Bishop Museum. Honolulu, 1909.

† Op. cit., p. 178.

so incessant and so titanic a warfare, solid masses may be compacted and floated on the surface of the liquid lava.

But the formation of a central cone at Halemaumau is not a very frequent occurrence while large, floating islands are comparatively common and it is clear that we must look to another cause for the origin of the majority of these interesting structures.

The island shown in fig. 1 was clearly seen to consist mainly of a mass of stratified, crystalline rock similar in appearance to that of the crater walls, and more particularly to that of the "black ledge"—an inner wall consolidated to the main wall during a former high level of the lava lake. This clue to the origin of the island was supported by the testimony of several residents, who affirmed that the mass of rock fell from the northeast sector of the black ledge in the early summer of 1910. The records, moreover, show several accounts of the formation of islands in this manner, of which I shall quote but one:—Mr. L. A. Thurston—an enthusiastic and indefatigable local observer, to whom the present writer is indebted for a mass of information and for innumerable courtesies—in his vivid description of the great subsidence in July, 1894,* wrote as follows: "Most of the falling rocks were immediately swallowed up by the lake, but when one of the great downfalls referred to occurred, it would not immediately sink, but would float off across the lake, a great floating island of rock."

Fig. 1.

Fig. 1. The Halemaumau Lava Lake with Floating Island, July, 1911.

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* Brigham, op. cit., p. 187.

We may conclude, therefore, that the majority of the larger and more important of these islands are formed in this simple manner, analogous, it will be seen, to the making of icebergs by the detachment of masses from a glacier on its entering the sea and, similarly, constituting one phase of a complete and recurrent cycle of events. The water of the sea, evaporated, falls as snow in the uplands, is consolidated to glacier ice which descends and is re-melted in the sea. The liquid lava rises in the conduit, is consolidated to the walls of the pit; the liquid subsides, the masses of rock break off and fall into the lake, floating about until swallowed up and re-melted in the seething cauldron.

The analogy fails, however, in regard to the flotation of the mass for, if the specific gravity of water in the solid state is less than in the liquid, the same cannot be said of lava. And this is especially true in the case of the lake material whose gas-vesiculated upper layers, as has been shown in the paper on Lava Fountains, offer but little resistance to the sinking of comparatively small pieces of the consolidated rock. It may well be considered strange that, where smaller blocks sink, a large mass of the same material, heavier than the liquid, should be floated upon it, and the first questions of the visiting tourist are generally "why does not the island sink and why does it not melt?" The answer is that it does sink and it does melt, but not all at once—it may be a matter of months rather than of moments. A number of causes may combine to bring about the initial flotation, and some of these will be effective in refloating the mass if submergence has taken place, which is inevitable at the beginning if the rock has acquired, to any considerable degree, the momentum of falling.

The mass of rock, in the first place, tends to float upon the lake of lava as a solid upon a liquid by which it is not *wet*, i. e. by reason of the latter's surface tension. At Etna the writer observed that huge bowlders which were incandescent and which therefore *amalgamated*, if the expression may be used, with the liquid lava, sank readily, while others, equally heavy but cold and black, floated high and dry upon the liquid whose surface tension was very great.

The rock may also enter the lake at the place of a rising lava current which will tend to buoy it up while, being cold and of sufficient mass to retain its temperature for a time, the lake material at once consolidates about it and forms a casing and a fringe which are comparatively light and under which the gases, constantly rising through the liquid, may accumulate and lend buoyancy to the whole.

The rock itself has been long exposed to the atmosphere and to moisture with consequent oxidation, etc., and when brought into contact with the liquid, basic lava at high temperature, chemical reaction ensues with evolution of gas from all points of the surface. This action is certainly effective in the reflotation of a sunken mass and may be compared with that seen when chips of zinc are dropped into a beaker of dilute acid and the evolved gas, clinging to the bits of metal, easily raises them to the surface.

The great buoyancy of gas bubbles in the liquid lava is amply demonstrated by the formation of imposing fountain domes, as described in a previous paper on that subject.

As to the re-fusion of the mass of the island, it will be evident that, under the normal condition of activity, the temperature of the immediate surface of the lake will be insufficient to accomplish this and instead, as we have seen, it is the lake material itself which tends to solidify in contact with the floating mass. But the prism of rock undoubtedly extends to a considerable distance below the surface, where the temperature and the chemical activity of the lava are much greater, and there the contact surfaces must be slowly eaten away. This action will be accelerated if, as frequently occurs, the mass of the island intercepts a path of upstreaming bubbles of juvenile gas whose temperature and chemical activity are very high and whose mechanical and fountain-forming powers as well will be directed against the opposing rock. There are also reasons for believing that certain portions of the rock act catalytically, facilitating the evolution of gas bubbles from the lake lava, the island thus conforming itself into a veritable focus of activity.

By some such means it would seem that a large cylindrical cavity was eroded vertically upwards from the bottom of the submerged mass to a point under the saddle between the two principal portions of the island and this became the seat of what was undoubtedly one of the most remarkable phenomena ever observed in this place of wonders, but of which the discussion must be deferred to a subsequent paper on the circulatory system of the lava lake. It may suffice to state here that the cavity was open at the surface level on either side of the saddle in the form of a grotto (fig. 2) within which fountain action produced a lower level of lava, as explained in the preceding paper on Lava Fountains. The result of this was an inpouring of the outside, surface liquid which still further lowered the inner level until a magnificent, free flowing, double cascade was formed and maintained for hours at a time. When it is realized that the surface lava was plunging downward from the level of the lake into a void in the submerged portion of an island which was, itself, floating freely in the same lake, it will be admitted that we have here a sufficiently interesting subject of investigation.

The roasting of the mass of rock, with its lower portion immersed in seething lava and its emergent part exposed to air and moisture, results in a complicated process of decomposition with evolution of vapors which, naturally, tend to rise in the fissures and lines of fracture, thus issuing principally from the summit of the island. Now, it is well known that such gas action inevitably enlarges the passages and it is interesting—and may be permissible—to imagine that, in time, these channels might be widened and extended to the liquid below in which case the ascending gases would bring up lava, and a true volcanic chimney would be established within an already formed containing edifice. This suggests the *possibility* of an ordinary mountain—formed, or in process of formation—becoming a volcano, whose ashes and lavas would soon obliterate the original contours.

Fig. 2.

Fig. 2. Showing grotto under central neck into which the surface lava was flowing and falling into a void below.

That the probabilities are all against this will be understood from the strongly compressed lower portion of the anticlinal type of fracture, i. e. a fracture in an anticlinal fold as contrasted with that of a synclinal fold which is open at the bottom to the intrusion—and therefore to the comparatively facile subsequent extrusion—of the volcanic materials from below. When it is considered how rarely, even under these comparatively favorable latter conditions, the eruptive forces succeed in establishing a vent at the earth's surface, it may well be considered improbable in the former case, but the suggestion conveyed by this smoking, floating island remains, nevertheless, an interesting possibility.

The eventual sinking of the islands is generally brought about by a process whose mode of action is as instructive as it is unlooked for and surprising. It might certainly be supposed that a solid mass in free flotation would be raised and lowered with the rise and fall of the level of the liquid in which it is suspended, yet such is not the case here. It is but another exemplification of the fact, upon which the writer has often had occasion to insist, viz. that a column of active lava must not be considered upon the basis of a simple liquid. It is true that a steady and continued rise of the lava will float an island upward, but in the case of those comparatively rapid oscillations of level which are frequent at the "turn of the tide" and especially so during a general subsidence of the lava column, the surface of the lake may rise or fall to the extent of from one to several meters without moving a large island vertically by so much as a single millimeter. The reason for this is that these rapid alternations in the level of the lake are due to a greater or lesser supply of gas—or of gas-charged lava—from below causing the surface to rise very much after the manner of boiling molasses. The lava at a certain distance below the surface, and in which the bulk of the island is presumably suspended, is not much affected and the island remains stationary while the rising surface emulsion overflows its shore, whereupon it sinks to some extent. If, instead of rising, the surface level is lowered, the island remains for a time with its line of shore emergent, but if the lava column as a whole is in process of subsiding, the island finally descends a little and is then carried by its momentum farther than it would otherwise have rested and so the next upward oscillation of the surface material engulfs the shore and still further sinks the whole. The seeming fact that the sinking of the island is effectuated during a general lowering of the lava column after floating many months on a generally rising lava receives additional explanation from the probability that the general subsidence is accompanied—if not caused—by a diminution in the supply of gases from below; which gases, as we have seen, lend buoyancy to the mass of rock. During the summer of 1911, the lava column reached its greatest height in the middle of July, when it stood seventy meters below the writer's station and dwelling on the east brink. Rapid oscillations began on the 17th and by the 22d the lake was in full subsidence. On the 31st the first great engulfment of the shore of the island occurred by which the island was sunk to the base of the solid original rock, no shore remaining at the surface. The immersion of this mass of relatively cool material caused an immediate diminution of activity over the entire lake, all fountain action was reduced, while a strong, continuous hissing sound evidenced the reaction of the lake material upon the previously exposed portions of the island.

No further relative sinking took place until August 9th when entire submergence was effected in the course of the day. This was due to a remarkable temporary rise of the lava corresponding to a favorable luni-solar position (opposition) to which influence the Kilauea lava column is very susceptible. Telephoto detail views were obtained of the sinking island, figs. 3 and 4 showing the degree of submergence at 10.30 A. M. and at 5.00 P. M.

Instead of sinking out of observation, however, the island remained at the surface and consolidated to itself a large flat mass of surface material. This condition continued until the 18th, when the island disappeared from observation, but in a manner so sensational and extraordinary that, were it not for the photographic record, the writer might almost hesitate to set forth, in writing, that which was actually seen. He feels that he cannot do better than transcribe from his original weekly report to the Honolulu Commercial Advertiser, which, written at the time of the occurrence, will have been, on that account, the more vividly descriptive:

"As stated in the report of last week, the visible island had been reduced to an almost flat area of crust lying adjacent to the east shore of the lake just below the station. Late on the evening of the 17th this crust was observed to be cracked and fissured in all directions, showing a bright glare below. As this clearly foreshadowed a change, a daylight view was eagerly awaited, but it so happened that a strong wind filled the pit with vapor and the lake could only be seen at rare intervals. Everything appeared to be normal, however, until 1.30 P. M. of the 18th, when, in a momentary clearing away of the smoke, an extraordinary object was seen, floating far out in the center of the lake. A huge, sausage-shaped, gas inflated balloon of black lava-glass—triangular or box-shaped at one end and cylindrical at the other—was making its way across the lake. A lava fountain, boiling continuously under the eastern end, gave the appearance of a screw propeller, and this most amazing contrivance seemed to be navigating the lake under its own power like a great whaleback steamer, or a black Zeppelin airship. Its length was not less than 170 feet and the cylindrical portion about 30 feet in diameter. After nearing the western bank it was driven back by a current and returned toward the station.

"Knowing that such a construction could not last, I made

Fig. 3.

Fig. 3. The Island sinking, Aug. 9, 1911. 10.30 a. m.

Fig. 4.

Fig. 4. The Island sinking, Aug. 9, 1911. 5.00 p. m.

desperate attempts to photograph it and succeeded in part, which is fortunate, as I believe that no one but myself and two Japanese were witnesses.

"The object no sooner reached the shore when two other fountains were formed under it—Old Faithful being withdrawn from its accustomed place to assist in the work of demolition—and the entire structure soon collapsed and sank out of sight beneath the now unbroken surface of the fiery lake.

"I have no doubt that the explanation of this phenomenon is as follows: The island was kept from sinking by the large, flat area of black crust and, on the breaking up of this, it began to sink. In so doing, a quantity of gas was evolved when the hot lava covered the rock and this blew the great cylindrical bubble which then continued to support the island, although below the surface, for the final tour of the lake. On the demolition of the great bubble the entire mass sank below the surface."

Fig. 5.

Fig. 5. The great inflated cylinder of black glass which formed over the sunken island, Aug. 18, 1911.

To this should be added that the cylinder (fig. 5) was evidently inflated and of great buoyancy, as shown by its almost wholly emergent flotation. The material was the black, vitreous rock which results from a rapid cooling of the lake lava. That the original island remained beneath the floating cylinder was proved by its partial emergence for a few moments (when it was also photographed) during the passage across the lake. The point of rock came up as clean and *dry* as a piece of wood out of mercury, showing that, while too hot to permit of the liquid lava's remaining and solidifying upon it, it had not yet reached the state of incandescence and therefore could not *amalgamate* with the lake material. This was after nine days of immersion, but always near the surface.

Of the island itself nothing more was seen, but on August

20th there were formed upon the surface the two islets shown in the telephoto view (fig. 6). It was suspected that their formation was due to the chilling effect of the original island, refloated to the surface but not emergent, and this was subsequently proved by a number of observations. It is highly probable, therefore, that the many instances, in the past, of the formation of new islets shortly after the disappearance of an island has been due, as in the present case, to the reflotation of the original mass.

In the detail view, fig. 6, the flow of the surface lava, from right to left, is well shown, giving to the two islets the appearance of buoys anchored in a tideway.

Fig. 6.

Fig. 6. Twin Islands, formed by chilling effect of the sunken mass.

The islets were repeatedly overwhelmed by upward oscillations of the surface lava and the writer, although not present at the time, believes that the mass of the island must have suffered fusion during the phase of abnormal activity which occurred towards the end of the year. This would give to the island as such, in the emergent state, an existence of about thirteen months with a subsurface, islet-forming condition lasting several months in addition.

It will be seen that the floating islands of Halemaumau, by their powerful influence upon the various activities of the lava lake, hold a not unimportant place among the phenomena of this most interesting volcano.

Posilipo, Naples, December, 1912.

Art. XXIV.—*On the Hydrolysis of Alkyl Metallic Sulphates*; by G. A. Linhart.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxli.]

IV. Sodium, Strontium, and Barium Esters in Alkaline Solutions.

Attention has been called to a paper[*] in which it is claimed that ethyl barium sulphate decomposes at a greater rate in water solution than in half normal aqueous hydrochloric acid, but not quite as rapidly as in normal acid. From these experimental results a differential equation too complex for integration is developed, and consequently no velocity constants[†] are calculated from the published experimental data. In the paper cited, similar discrepancies appear in Kremann's work with barium ethyl sulphate in alkaline solution.

From a long series of carefully executed reaction velocity measurements in acid, water and alkaline solutions[‡] it is evident that not only are Kremann's experimental data unreliable, but likewise his theory must be incorrect. Assuming that the $\overline{OH}$ ions of the sodium hydroxide used have no appreciable effect on the ethyl barium sulphate in the course of hydrolysis, Kremann considers the reaction to be of the first order and represents it by the following equations:

$$\text{“}Ba(C_2H_5SO_4)_2 + 2H_2O = BaSO_4 + 2C_2H_5OH + H_2SO_4$$
$$Ba(C_2H_5SO_4)_2 + H_2SO_4 + 2NaOH = BaSO_4 + 2NaC_2H_5SO_4 + 2H_2O.\text{”}$$

The formation of barium sulphate, Kremann states, is due chiefly to these two reactions, since, according to his observation, the ethyl sodium sulphate resulting from the interaction of the sodium hydroxide and the ethyl sulphuric acid liberated in the course of the hydrolysis of the barium ethyl sulphate does not undergo any appreciable transformation into sodium sulphate during a period of eight days at temperatures of 55° and 66° at which his hydrolyses were made. From a preliminary experiment[§] at 60° I found that ethyl sodium sulphate is transformed into sodium sulphate during a period of eight days to the extent of about 16 per cent. In his conclu-

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[*] R. Kremann, Monatsh. für Chem. (3), xxxi, 165.

[†] It is often possible in such cases to calculate constants directly from the differential equation with a sufficient degree of accuracy by substituting mean values for short time intervals.

[‡] This Journal, xxxii, 53; xxxiv, 289 and 539.

[§] See p. 288.

sion Kremann states that the reaction proceeds to a very small degree according to the following equation:

$$\text{“}Ba(C_2H_5SO_4)_2 + 4NaOH = BaSO_4 + Na_2SO_4 + 2C_2H_5OH + 2H_2O\text{”}$$

and he considers it to be a reaction of the fifth order.* It is evident that in place of the $2H_2O$ there should be 2NaOH or

$$Ba(C_2H_5SO_4)_2 + 2NaOH = BaSO_4 + Na_2SO_4 + 2C_2H_5OH,$$

which is plainly a reaction of the third order.

Theory.—When a solution of ethyl barium sulphate (one mol per liter) is mixed with a solution of sodium hydroxide free from CO_2 (two mols per liter) in equal volumes, barium hydroxide is at once precipitated in crystalline form. This is due to the fact that barium hydroxide is not soluble to that extent at room temperature, especially in the presence of sodium hydroxide. We may, therefore, assume that when equal volumes of ethyl barium sulphate (0·6 gram equivalents per liter) and sodium hydroxide (2·7 gram equivalents per liter) are mixed, some of the ethyl barium sulphate is changed to barium hydroxide according to:

$$Ba(C_2H_5SO_4)_2 + 2NaOH \rightleftarrows 2NaC_2H_5SO_4 + Ba(OH)_2$$

The probable reactions, therefore, taking place in the saponification of the two esters by the two bases may be represented by the following equations:

(*a*) $Ba(C_2H_5SO_4)_2 + NaOH = BaSO_4 + NaC_2H_5SO_4 + C_2H_5OH,$
(*b*) $Ba(C_2H_5SO_4)_2 + Ba(OH)_2 = 2BaSO_4 + 2C_2H_5OH,$
(*c*) $NaC_2H_5SO_4 + Ba(OH)_2 = BaSO_4 + NaOH + C_2H_5OH,$
(*d*) $NaC_2H_5SO_4 + NaOH = Na_2SO_4 + C_2H_5OH$;

the sodium sulphate immediately reacts with the ethyl barium sulphate and barium hydroxide:

$$Ba(C_2H_5SO_4)_2 + Na_2SO_4 = BaSO_4 + 2NaC_2H_5SO_4, \text{ and}$$
$$Ba(OH)_2 + Na_2SO_4 = BaSO_4 + 2NaOH.$$

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* “— Würde hingegen der Zerfall von ätylschwefelsaurem Baryt hauptsächlich durch NaOH direkt erfolgen, wäre diese Reaktion nach

$$Ba(C_2H_5SO_4)_2 + 4NaOH = BaSO_4 + Na_2SO_4 + 2C_2H_5OH + 2H_2O \qquad (7)$$

zu formulieren. Es würde also eine Reaktion fünfter Ordnung resultieren. Die Tatsache, dass der Reaktionsverlauf anfänglich annähernd durch eine Gleichung erster Ordnung darstellbar ist, spricht für die Unwarscheinlichkeit der Annahme der Gleichung 7. Naturlich soll nicht geleugnet werden, dass zu gewissem, aber untergeordnetem Betrag die Reaktion des Zerfalles von äthylschwefelsaurem Baryt auch nach Gleichung 7 vonstatten gehen kann. Hierauf würde sogar die Tatsache deuten, dass die anfängliche Reaktionsgeschwindigkeit mit steigender Konzentration des NaOH stärker zunimmt als der direkten Proportionalität zwischen Reaktionsgeschwindigkeit und Konzentration des NaOH entspricht.” R. Kremann, Monatsh. für Chem. (3), xxxi, 175.

If the reactions are considered strictly ionic they can be represented by a single equation:

$$C_2H_5SO_4' + OH' \longrightarrow C_2H_5OH + SO_4''.$$

In either case, whether the reactions are considered to be molecular or ionic, no concordant constants would be expected, for the equilibrium is continuously shifting from lower to more highly dissociated substances as the barium ions are removed from solution. It might be supposed that this would tend to accelerate the reaction slightly, and thus mislead one to consider the reaction to be of the first order. However, Kremann's constants cannot be used to confirm the above supposition, as he did not use the proper formula in his calculations, for it is evident from the above ionic equation that for every gram equivalent of ester decomposed there are formed two gram equivalents of sulphate. Therefore, the concentration of ester at any time t should be represented by $A - \frac{1}{2}x$ instead of by $A - x$. This leads to the expression

$$\frac{dx}{dt} = K(A - \tfrac{1}{2}x)$$

which on integration gives

$$K = \frac{2 \times 2 \cdot 3}{t} \log \frac{A}{A - \frac{1}{2}x}$$

where A denotes the initial concentration of ester and x the amount of barium sulphate formed in time t, both expressed in gram equivalents per liter.

In the first four columns of Tables I and II are given Kremann's results as published in the article cited. The constants published in that paper he calculated from a formula* derived on the assumption that the hydrogen ions of the water react directly with the barium ester, and that the $\overline{OH}$ ions of the sodium hydroxide merely neutralize the ethyl sulphuric acid, forming ethyl sodium sulphate which, according to his observations, is not transformed to sodium sulphate during the entire periods indicated in his tables below under t. In the fifth column are given the constants calculated from the correct formula† if the reaction were of the first order, and in the sixth column, if the reaction is considered to be of the second order.‡ It is evident from the figures in Table I, column 6, that if the reaction is of the second order, fairer velocity constants are obtained if Kremann's experimental results are substituted in the correct formula.‡ No concordant constants, however, can be obtained from his results in Table II; there is a gradual decrease of about eighteen per cent even if the reaction is considered to be of the third order.§

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* See page 286, note *.
† See page 286, note †.
‡ See page 286, note ‡.
§ See page 284.

TABLE I.

T = 55° b = 20$^{\mathrm{cm}^3}$ of normal NaOH ∥

t in minutes	$BaSO_4$ in grams	$BaSO_4$ in cm³ 0·1 mol	K*	K†	K‡
10020	0·146	6·3	$21{\cdot}4\times10^{-6}$	$20{\cdot}2\times10^{-6}$	$20{\cdot}5\times10^{-8}$
20340	0·249	10·7	$20{\cdot}0\times10^{-6}$	$17{\cdot}6\times10^{-6}$	$18{\cdot}0\times10^{-8}$
∞	0·744	$32{\cdot}6=a$			
				b = 20$^{\mathrm{cm}^3}$ of 0·5 normal NaOH §	
10020	0·062	2·7	$8{\cdot}5\times10^{-6}$	$8{\cdot}42\times10^{-6}$	$17{\cdot}1\times10^{-8}$
20340	0·110	4·7	$7{\cdot}6\times10^{-6}$	$7{\cdot}36\times10^{-6}$	$15{\cdot}0\times10^{-8}$
29040	0·163	7·0	$8{\cdot}3\times10^{-6}$	$7{\cdot}82\times10^{-6}$	$16{\cdot}2\times10^{-8}$
39120	0·210	9·0	$8{\cdot}3\times10^{-6}$	$7{\cdot}59\times10^{-6}$	$16{\cdot}2\times10^{-8}$
∞	0·744	$32{\cdot}6=a$			

TABLE II.

T = 66° b = 20$^{\mathrm{cm}^3}$ of normal NaOH ∥

t in minutes	$BaSO_4$ in grams	$BaSO_4$ in cm³ 0·1 mol	K*	K†	K‡
600	0·032	1·4	74×10^{-6}	$73{\cdot}7\times10^{-6}$	$72{\cdot}1\times10^{-8}$
1440	0·074	3·2	72×10^{-6}	$69{\cdot}9\times10^{-6}$	$70{\cdot}0\times10^{-8}$
8310	0·319	13·7	66×10^{-6}	$56{\cdot}6\times10^{-6}$	$58{\cdot}6\times10^{-8}$
10690	0·371	15·9	60×10^{-6}	$52{\cdot}4\times10^{-2}$	$54{\cdot}4\times10^{-8}$
∞	0·744	$32{\cdot}6=a$			

From theoretical considerations, as already pointed out, it might be supposed that the discrepancies in Kremann's constants, especially those in Table II, are due to the fact that he used sodium hydroxide for the saponification of the ethyl barium sulphate. In order, therefore, to avoid these difficulties, the several esters treated of in this article were saponified in hydroxides whose metallic element was either the same as, or similar to, the one contained in the ester. The reaction taking place under these conditions may be represented by the general equation:

$$*\,K = \frac{2{\cdot}3}{t}\log\frac{a}{a-x} \qquad \dagger\,K = \frac{2\times2{\cdot}3}{t}\log\frac{a}{a-\frac{1}{2}x}$$

$$\ddagger\,K = \frac{2{\cdot}3\times2}{(a-b)\,t}\log\frac{(a-\frac{1}{2}x)\,b}{(b-\frac{1}{2}x)\,a}$$

∥ 20 cm³ of normal NaOH $\bumpeq$ 100 cm³ of 0·2 normal NaOH.
§ 20 cm³ of 0·5 normal NaOH $\bumpeq$ 50 cm³ of 0·2 normal NaOH.

$MRSO_4 + MOH = M_2SO_4 + ROH$, if M has a valence of one, and $M(RSO_4)_2 + M(OH)_2 = 2\,MSO_4 + 2ROH$, if M has a valence of two.

This is plainly a reaction of the second order leading to the mathematical expression

$\frac{dx}{dt} = K\,(A - \frac{1}{2}\,x)\,(B - \frac{1}{2}\,x)$, where A, B, and x are all expressed in gram equivalents per liter, A and B denoting the initial concentrations of the reacting substances respectively and x the barium sulphate precipitated in time t. On integration the above equation gives for the velocity constant

$$K = \frac{2 \times 2{\cdot}3}{(A - B)t} \log \frac{(A - \frac{1}{2}\,x)B}{(B - \frac{1}{2}\,x)\,A}$$

$A - \frac{1}{2}\,x$ and $B - \frac{1}{2}x$ are used instead of $A - x$ and $B - x$ since for every gram equivalent of ester or base transformed there are formed two gram equivalents of sulphate.

Experimental Part.—For the saponification of the ethyl sodium sulphate, silver tubes about 12^{cm} in length and of about 40^{cm^3} capacity were used. These tubes were placed in glass tubes which fitted loosely over them. The glass tubes were then constricted at about one inch above the top of the silver tube to a size just large enough to allow a finely drawn out tube to go through and the displaced air to escape. This drawn out tube was connected by means of a piece of rubber tubing to a burette which was attached to a bottle containing the CO_2 free sodium hydroxide. Each silver tube was provided with a flat coil of fine platinum wire, the inner end of which was bent upwards and projected about a half inch out of the mouth of the silver tube. After 10^{cm^3} of 0·6N ethyl sodium sulphate were introduced by means of a carefully calibrated pipette, and also 10^{cm^3} of the CO_2 free sodium hydroxide from the burette by means of the drawn out tube connected with it, the projecting platinum wire was grasped with a pair of long pincers and slowly moved up and down until the two dissolved substances were well mixed. The tubes were then sealed, cooled and submerged in the thermostat at 60°. A thin piece of cork had to be placed between the walls of the silver and the glass to keep the top of the silver tube from touching the glass. This was found necessary as the liquid, although about 4^{cm} from the top, would gradually rise after being in the thermostat for several days and attack the glass if the silver tubes were allowed to lean against it.

Before treating the sodium sulphate resulting from the saponification of the ethyl sodium sulphate by the sodium hydroxide, with a solution of barium chloride which had to be done in the cold (room temperature), the excess of sodium hydroxide was neutralized with hydrochloric acid and made slightly acid. The barium sulphate precipitated under these conditions carried down considerable sodium chloride. In order to remove as far as possible this included sodium chloride, the precipitated barium sulphate was filtered through an ignited and weighed perforated platinum crucible, thoroughly washed with hot water and then ignited. After cooling the precipitate was again washed with hot water until the wash-water no longer reacted with silver nitrate. The ignition was then repeated and the barium sulphate again washed with hot water after cooling. In this manner, practically all the sodium chloride was removed. The crucible was then heated to redness, allowed to cool and weighed. The barium sulphate resulting was used in calculating the velocity constants in place of sodium sulphate, since this weight calculated to gram equivalents per liter is exactly equivalent to the sodium sulphate resulting from the saponification.

The saponification of the barium and strontium esters with barium hydroxide was carried out in glass tubes. In these cases it was found that, although the barium hydroxide began at first to attack the glass, a thin film of barium sulphate or silicate or probably of both was formed on the walls of the tubes, thus preventing further corrosion. In these experiments, as in the above, the barium hydroxide was neutralized with hydrochloric acid in slight excess, and the precipitated barium sulphate was thoroughly mixed to decompose any barium hydroxide that might have adhered to the precipitate. The precipitate was then treated and estimated in the manner described above.

Experimental Results.

T = 60°

Ethyl sodium sulphate 0·3 grm. equiv. per l. = B
Sodium hydroxide 1·35 " " " l. = A

t	$BaSO_4 = x$		K*	K†
in hours	in grams	in grm. equiv.	1st order	2d order
200·0	0·2564	0·1099	0·00242	0·00211
603·0	0·6100	0·2614	0·00190	0·00208
986·0	0·8400	0·3600	0·00186	0·00209
∞	1·4004	0·6000		

Methyl strontium sulphate 0·3057 grm. equiv. per l. = A
Barium hydroxide 0·2757 " " " l. = B

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* See page 285.

† See page 287.

t	‡$BaSO_4 = x$		K*	K†
in hours	in grams	in grm. equiv.	1st order	2d order
44·2	0·1550	0·0664	0·00520	0·0200
65·5	0·2110	0·0904	0·00488	0·0193
135·2	0·3717	0·1593	0·00446	0·0193
231·7	0·5188	0·2223	0·00390	0·0189
∞	0·6435	0·2757		

Methyl barium sulphate 0·3 grm. equiv. per l. = B
Barium hydroxide 0·4441 " " " l. = A

t	$BaSO_4 = x$		K*	K†
in hours	in grams	in grm. equiv.	1st order	2d order
16·5	0·0954	0·0409	0·00856	0·0197
29·0	0·1614	0·0692	0·00842	0·0198
44·5	0·2352	0·1008	0·00828	0·0198
64·7	0·3174	0·1360	0·00796	0·0195
94·5	0·4288	0·1846	0·00777	0·0198
136·0	0·5494	0·2354	0·00736	0·0193
205·0	0·7046	0·3019	0·00681	0·0191
257·0	0·8004	0·3429	0·00658	0·0194
354·0	0·9326	0·3991	0·00616	0·0195
689·0	1·2000	0·5014	0·00524	0·0195
∞	1·4004	0·6000		

Summary.—The experimental results lead to the following conclusions:

1. Kremann's theory that the decomposition of ethyl barium sulphate in alkaline solution is a reaction of the first order is necessarily wrong, since it is based on his observation that the sodium ethyl sulphate does not undergo any transformation to sodium sulphate during the entire course of the reaction, and on his assumption that the $\overline{\text{OH}}$ ions have no appreciable effect on the rate of the reaction, except to a very small degree according to the following equation:

"$Ba(C_2H_5SO_4)_2 + 4NaOH = BaSO_4 + Na_2SO_4 + 2C_2H_5OH + 2H_2O$."

2. In order to verify the assumption that the reaction is of the second order, experiments were carried out with bases having the metallic element similar to or the same as the one contained in the ester. From these experiments concordant constants are obtained if the experimental results are substituted in a formula representing a reaction of the second order, while if substituted in a formula representing a reaction of the first order, which according to Kremann should give fairly concordant constants, a gradual decrease of about 40 per cent is observed.

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[*] See page 285. [†] See page 287.

[‡] Since strontium sulphate is somewhat soluble in water, it is instantaneously and quantitatively removed from the reacting system, by combining with barium hydroxide present to form barium sulphate. It is the weights of this barium sulphate equivalent to the strontium sulphate expressed in gram equivalents per liter which are given in the table under grams and gram equivalents.

ART. XXV.—*Delafossite, a Cuprous Metaferrite from Bisbee, Arizona;* by AUSTIN F. ROGERS. With an analysis by G. S. BOHART.

MR. WM. L. TOVOTE, geologist of the Old Dominion Mining Company of Globe, Arizona, kindly sent me for identification and description some specimens of what was thought to be a new mineral from Bisbee, Arizona. The mineral is hexagonal in crystallization, and on analysis proves to have the formula $CuFeO_2$. In 1873 Friedel* described a Siberian mineral with the composition $Cu_2O . Fe_2O_3$, to which he gave the name delafossite. The Bisbee mineral must be referred to delafossite, and though not a new mineral the results obtained warrant the establishment of delafossite as a distinct mineral species.†

FIG. 1.

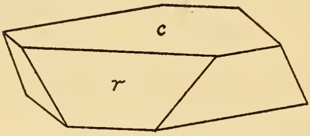
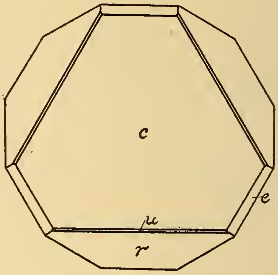


FIG. 2.



Occurrence.—The mineral under discussion was found by Mr. Tovote in a stope above the 14th level of the Hoatson shaft of the Calumet and Arizona property near the Copper Queen line. According to Mr. Tovote‡ it occurred in a great mass of white kaolin and ferruginous clay at about the lowest zone of oxidization. The surrounding country rock is limestone. The associated minerals include copper, cuprite, and hematite; the hand specimens contain copper and hematite.

Crystallography.—The mineral is found in more or less distinct crystals and subbotryoidal crystal aggregates on massive hematite. The crystals are hexagonal and greatly resemble hematite crystals, for they consist of a pinacoid $\{0001\}$ with a rhombohedron $\{10\bar{1}1\}$, and are tabular to equidimensional in habit. There are also composite prismatic crystals with concave pinacoidal faces which suggest the "eisenrosen." Fig. 1 represents a typical crystal. The hexagonal prism $\{10\bar{1}0\}$,

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* Comptes Rendus, vol. lxxvii, p. 211.

† In Dana's System of Mineralogy, 6th edition (p. 259), and in Hintze's Handbuch der Mineralogie (vol. i, p. 1939) it is included in the Appendix to Oxides.

‡ Mining and Scientific Press, vol. cii, p. 206, 1911.

another positive rhombohedron $\{ho\bar{h}l\}$, and a negative rhombohedron $\{oh\bar{h}l\}$, are also present. These are probably $u\{10\bar{1}4\}$ and $e\{01\bar{1}2\}$ respectively. Fig. 2 is a plan showing these doubtful forms.

Unfortunately the crystals are not suitable for goniometrical measurements. Of the various forms the basal pinacoid alone gives an image when mounted on the goniometer. The unit rhombohedral faces are composite and give no images at all. Consequently the reflections from the faces had to be relied upon, and the angles of course are only approximations. The average of five measurements of the angle $(0001:10\bar{1}1)$ on one crystal gave 65°, and the average of ten measurements of the same angle on another crystal gave 67°. Taking the average of these two averages we have 66° as an approximate value. The value of the *c*-axis for this angle is 1·94. The angle $(10\bar{1}1:01\bar{1}\bar{1})$ was also measured; the average of five measurements is 76° 45′. The calculated value, assuming the fundamental angle $(0001:10\bar{1}1)$ to be 66°, for $(10\bar{1}1:01\bar{1}\bar{1})$ is 75° 26′. Several contact twins with $\{0001\}$ as the twin-plane were noted. There is an imperfect cleavage parallel to the prism $\{10\bar{1}0\}$.

Physical Properties.—The color is black; the streak, black; the luster, metallic; and the hardness, about 5½. The mineral is brittle and non-magnetic, but is easily fusible and becomes magnetic when heated on charcoal. The usual pyrognostic tests for copper and iron were obtained. The mineral is easily soluble in hydrochloric and sulphuric acids, but is soluble with difficulty, if at all, in nitric acid.

Chemical Analysis.—A chemical analysis of the pure mineral (practically free from hematite) made by Mr. G. S. Bohart of the Chemistry department of Stanford University gave the following results:

	No. 1	No. 2	Average	Ratio	Theory $CuFeO_2$
Cu =	41·24	41·39	41·32	0·652	42·01
Fe =	37·22	37·30	37·26	0·667	36·85
Insol. = (Hematite)	0·25	0·17	0·21	----	----
O = (by difference)	21·29	21·14	21·21	1·325	21·14
	100·00	100·00	100·00	-----	100·00

The ratios are very closely Cu : Fe : O = 1 : 1 : 2. The slight excess of iron over copper may be explained by the fact that the analyzed sample contained a small amount of hematite, a part of which was soluble in sulphuric acid, the acid used to get the mineral in solution. The empirical formula of the delafossite from Bisbee is $CuFeO_2$, which is equivalent to $Cu_2O . Fe_2O_3$, obtained for the Siberian mineral by Friedel. Groth* gives the formula $Cu''_2O(FeO_2)_2$ on account of the supposed analogy with ludwigite, $Mg_2O(FeO_2)(BO_2)$.

Chemical Constitution.—When we attempt to establish the chemical constitution of the mineral there are serious difficulties. The delafossite, it is safe to assume, is a copper salt of an iron acid and not a mixture of copper and iron oxides. It may be cuprous metaferrite, $Cu'Fe'''O_2$, a salt of $HFeO_2$, (H_3FeO_3-H_2O), metaferrous acid, or a cupric salt ($Cu''Fe''O_2$) of H_2FeO_2, a possible acid which we may call hypoferrous acid. A number of metaferrites are known, but there is no record of hypoferrites.

Both the hydrochloric and sulphuric acid solutions of the pure mineral give distinct tests for ferric and ferrous ions with potassium ferrocyanide and potassium ferricyanide respectively. These tests were made with coarsely crushed fragments of the pure mineral free from hematite, so that the ferric iron test was not due to oxidation by fine grinding or to admixed hematite.

These tests indicate either that both ferrous and ferric iron are originally present in the mineral or that in the act of solution a change in the valence of the iron takes place. The compound $Cu'Fe'''O_2 . Cu''Fe''O_2$ or $Cu_2O . CuO . FeO . Fe_2O_3$ also has the empirical formula $CuFeO_2$ and would account for both the ferrous and ferric iron tests, but a formula of this kind is very improbable. It is more reasonable to suppose that a change of valence of iron has taken place during solution. A few rough experiments by the writer confirm this idea. A mixture of cupric sulphate and ferrous sulphate solution gives a decided test for ferric iron. This recalls the blowpipe test for ferrous iron.†

Stokes‡ gives the reaction: $Cu''+Fe'' \rightleftarrows Cu'+Fe'''$, which he established by experimental proof. The reversibility of this reaction is also confirmed by experiments made by the writer. Cuprous oxide and ferric oxide dissolve in sulphuric acid to a green solution, which gives tests for both ferrous and ferric iron. The reversibility of the reaction established by Stokes explains why tests for both ferrous and ferric iron are obtained from acid solutions of delafossite.

We are still left in doubt as to whether the formula of delafossite is $Cu'Fe'''O_2$ or $Cu''Fe''O_2$. Either formula will account for the observed facts. Mr. Bohart made a quantita-

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* Tabellarische Uebersicht der Mineralien, 4th ed., p. 79, 1898.

† A borax bead made blue with CuO is changed in a neutral flame to opaque red (Cu_2O) by ferrous iron. The equation is: $2CuO+2FeO=Cu_2O+Fe_2O_3$.

‡ Bull. 186, U. S. Geological Survey, p. 44, 1906.

tive determination of ferrous iron by titrating the sulphuric acid solution of the mineral with potassium permanganate solution and obtained results which, calculated, give 34·10 and 34·62 as the percentages of ferrous iron. This might indicate that all the iron was in the ferrous state, about 2½ per cent having been oxidized by fine grinding, were it not for the fact that a solution of the coarsely crushed mineral gave distinct tests for ferric iron. Another fact to be considered in this connection is that cuprous ions will also decolorize potassium permanganate solution. The results obtained by Mr. Bohart are due to the combined effect of the ferrous and cuprous ions and there is no way of determining the effect of the ferrous ion alone. Copper, of course, should be removed when titrating an iron solution with permanganate, but it could not be done in this case without changing the condition of the iron.

My colleague, Professor G. H. Clevenger, suggested that the original condition of the copper in the mineral under discussion might be determined by using as a reagent silver sulphate solution. In the Ziervogel process (a metallurgical process of silver extraction) the presence of cuprous oxide, an undesirable constituent, is indicated by testing the product with silver sulphate solution, in which case thin flakes of metallic silver appear. This is known as the "spangle reaction."*

The powdered delafossite when heated with a slightly acidulated silver sulphate solution gave a beautiful spangle reaction after standing about two days. Ferrous iron also gives this reaction, as the writer proved with siderite. In fact, almost any reducing agent may give it. But in delafossite the only possibilities to consider are cuprous copper and ferrous iron. Now, in delafossite the iron is, in all probability, combined with the oxygen as a radical and it probably does not act as iron, but only as a radical. The composition of delafossite, then, is probably cuprous metaferrite, $Cu'Fe'''O_2$.

Chalcopyrite, $CuFeS_2$, and magnetite, $FeFe_2O_4$, also give the spangle reaction with silver sulphate. With chalcopyrite it is the cuprous copper, and with magnetite it is the ferrous iron that acts as a reducing agent. This would indicate that these minerals are, respectively, cuprous metasulfoferrite, $Cu'Fe'''S_2$, and ferrous metaferrite, $Fe'Fe_2'''O_4$. Some mineralogists have considered these as the most probable formulæ; the spangle reaction, perhaps, makes it more certain.

Similar Compounds.—Magnetite, $FeFe_2O_4$, franklinite, $(Zn, Fe)Fe_2O_4$, magnesioferrite, $MgFe_2O_4$, and jacobsite, $MnFe_2O_4$, are well-known metaferrites, all isometric in crystallization.

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* Egleston, The Metallurgy of Silver, Gold and Mercury in the United States, vol. i, p. 134, 1887.

Cupric metaferrite, $CuFe_2O_4$, is known* but not its crystal form. One would expect it to be isometric.

Not many cuprous compounds are known, but they seem to be related to alkali compounds rather than to the dyad metal compounds. CuCl, CuBr, and CuI are isometric like the sodium and potassium haloids. Sodium metaferrite, $NaFeO_2$, crystallizes in hexagonal plates and rhombohedral plates according to van Bemmelen and Klobbie.† This compound and delafossite are perhaps isomorphous. Chalcopyrite, $CuFeS_2$, analogous to $CuFeO_2$, is tetragonal, but the sulpho-salts are not usually isomorphous with the corresponding oxy-salts.

Identity with Delafossite.—As the Bisbee mineral is a pure, well-crystallized compound of definite chemical composition, it is entitled to recognition as a distinct mineral species. It is hexagonal-rhombohedral in crystallization and has the empirical composition $CuFeO_2$. It agrees with a Siberian mineral described by Friedel under the name of delafossite except in cleavage and hardness. As these properties are not fundamental the Bisbee mineral is referred to delafossite and the evidence, it is believed, is complete enough to establish delafossite as a definite independent mineral species. It is probably cuprous metaferrite, $Cu'Fe'''O_2$.

Note.—Since writing the above Mr. Tovote has sent me several additional specimens of delafossite from Bisbee. One of them is a soft, black, graphite-like mineral which marks paper and has a lamellar structure. It gives the same chemical tests as the crystallized delafossite and agrees with the description of the Siberian mineral. The lamellar structure may account for the apparent cleavage and also for the inferior hardness. Hematite presents an analogous case, for some varieties are very soft and have an apparent cleavage in one direction which is due to lamellar structure.

Stanford University in California,
November, 1912.

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* List, Berichte d. Deutsch. Chem. Ges., vol. xi, p. 1512, 1878.

† Jour. prakt. Chemie, vol. cliv, p. 509, 1892.

ART. XXVI.—*On the Electric Charges of the α- and β-Rays;* by JEAN DANYSZ and WILLIAM DUANE.

THIS article contains a description of experiments designed to measure the electric charges carried by the α- and β-rays from a given quantity of a radio-active substance. The experiments were begun several years ago at the suggestion of Madame Curie, but were discontinued pending the construction of a satisfactory source of rays and the preparation of the international standard of radium.

A good source of rays should admit of easy comparison with the radium standard, and should be so constructed that all the rays produced emerge from it. Radium is not satisfactory because the substance itself absorbs an imperfectly known fraction of its own rays, and because it is not easy to determine just how much emanation and active deposit there is in the salt at every instant of time. The active deposit, radium ABC, although perfect from the point of view of absorption, is not convenient on account of its rapid rate of decay, and also because it is not easy to deposit very large quantities on a small surface even in a strong electric field. We have chosen the emanation of radium with the active deposit in equilibrium with it (radium ABC) as our source of rays for the following reasons: (*a*) it is possible to measure a quantity of emanation in terms of the amount actually present in the international standard of radium with considerable accuracy by means of the γ-ray methods, (*b*) the rate of decay of the emanation with the time is very accurately known, (*c*) the rate of decay is so slow that a given quantity can be used for a long time before it becomes too small, (*d*) the masses of the active substances are so small that the α- and β-rays are not appreciably absorbed by them, and (*e*) a large quantity of emanation and active deposit can be compressed into a very small space, thus producing very nearly a point source of intense radiation.

The emanation being a gas must be confined in something, and we have employed small spheres of glass with very thin walls.* After its preparation (for method of blowing spheres see references) the little sphere is sealed on to the tubes employed in the purification of the emanation, and a little bubble of emanation is pushed by mercury into the upper part of the sphere. The bubbles have volumes of about $\cdot 5^{\mathrm{mm}^3}$, and the spheres about 14^{mm^3}, so that a bubble is flattened out between a surface of glass and one of mercury, each of which

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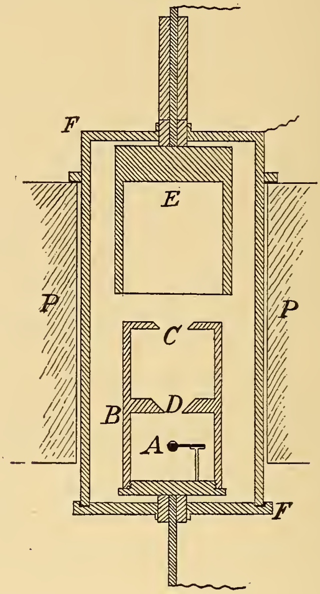
* Such point sources of rays have been employed by Duane and Lind (Comptes rendus, July, 1911, Radium, 1912, and Sitz. der Akad. Wien, Dec., 1911).

is roughly horizontal. The absorbing power of the glass covering each of the bubbles of emanation used in the experiments was estimated by measuring the length of path of the α-rays in the air after they had emerged from the spheres. These experiments indicated that the glass in its thinnest place absorbed the rays about as one centimeter of air would. It is possible that the glass was not everywhere as thin as this, but experiments described below proved that all the α-particles projected vertically upward emerged from the spheres.

Fig. 1.



To produce a well-defined beam containing a known fraction of the α-rays, the sphere was supported at A (fig. 1) inside a metal cylinder B with thick walls. The distance from the bubble of emanation to the top of the cylinder was 4·055^{cm}, and the top contained a circular hole 1·025^{cm} in diameter, so that the ratio of the α-rays passing out through the hole to the total number of α-rays supposed distributed uniformly in all directions around the source was ·00400.

In order to separate the charges of the α- and β-rays from each other a diaphragm D with a circular hole ·602^{cm} in diameter was fastened in the cylinder at a distance of 2·99^{cm} from the top, and the apparatus was placed between the poles P of a large electromagnet, the lines of force of the field being horizontal, and, therefore, normal to the axis of the cylinder. The magnetic field deflects the rays, and a study of the geometry of the figure shows that none of the rays passing through C are stopped by the diaphragm D, if the radii of curvature of their paths are greater than 10^{cm}: and that no ray for which the radius of curvature is less than $3{\cdot}8^{cm}$ can pass through C. The magnetic field strength was measured by means of a standardized fluxmeter, and attained a maximum value in the experiments of about 8000 gauss.

All the rays passing through the hole C enter the metal cylindrical box E connected to a piezo-electric quartz and an electrometer, by means of which their charges are measured. The top of the box E is made thick so as to stop the greater portion of the γ-rays, which, if they came out at the top might produce secondary rays in sufficient quantity to alter perceptibly the charge of electricity measured. The bottom of the box consists of a thin sheet of aluminium; its distance above the cylinder B being about 8^{mm}.

To protect the wires and measuring instruments from the penetrating γ-rays the quartz and electrometer were placed in such a position that the rays had to pass through the long pole piece of the electromagnet before reaching them, and all wire connections were imbedded in paraffine or ebonite, which were covered in turn with metal tubes put to earth.

The piezo-electric quartz had been calibrated some years before by means of a standard condenser and standard cadmium cells. It was recalibrated by measuring the same ionization current once by the quartz and again by a galvanometer, the figure of merit of which had been determined by means of standard resistances and standard cells. A weight of one kilogram suspended from the quartz produced a displacement of 5·86 electrostatic units of electricity.

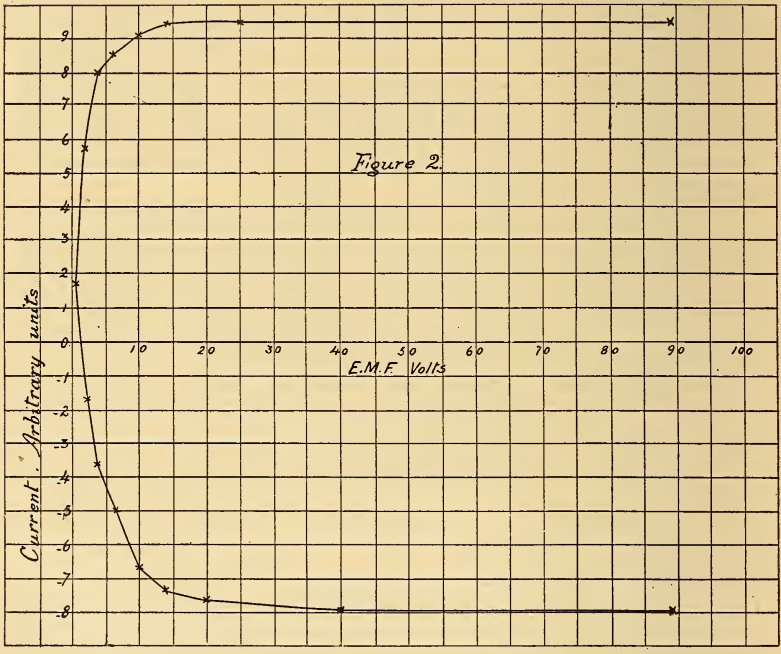
The two cylindrical boxes B and E were supported inside a larger metal box F, in which a high vacuum was produced by means of a Gaede mercury pump. The cylinder B (as well as E) was insulated from the box F so that it could be charged to any desired potential, while the box F remained always put to earth.

A series of measurements were made with the hole C covered with a sheet of aluminium $\cdot004^{mm}$ thick, and with the cylinder B raised to different potentials. The curves in figure 2 represent the results. It will be noticed that both positive and negative currents reach maximum values for electric fields of a few volts, the negative potential required to produce saturation being a trifle larger than the positive.

These currents are not due to ordinary ionization in the residual gas, for ionization currents at such low pressures would be saturated by very small electric forces. Further special series of experiments have shown that the gas pressure has no effect on the currents provided it is below certain values easily obtainable with the Gaede pump. The use of carbon and liquid air to reduce the pressure below that reached with the pump was found to be quite unnecessary.

The currents are undoubtedly the results of the superposition of the charges carried by the secondary rays due to the *α*-rays on those carried by the *α*- and *β*-rays themselves. These secondary rays are produced at the surfaces of the sheets of aluminium, both that attached to the bottom of E and that covering the hole C. Only those between the sheets count, for the others remain within their respective boxes and do not alter the charge received by the box E. If there is no difference of potential between the boxes B and E the secondary rays projected down from the upper sheet more or less balance those projected upward from the lower sheet. One cannot be sure, however, that there is an exact balance, and that the charge measured under these conditions is the charge of the *α*- and *β*-rays themselves, for the *α*-rays traverse the sheets upward

Fig. 2.



and may produce more secondary rays in the direction of their own motion than in the reverse direction, or vice versa; and further, even when the two boxes are at the same potential there may be a small electric field between them due to the Volta electromotive forces.

If the cylinder B is charged positively the negatively charged secondary rays are pulled downward, thus producing a positive current upward toward the box E, and when the field is so strong that the current has reached its maximum value all the secondary rays projected upward from the lower sheet are stopped by the electric force. If the cylinder B is charged negatively the secondary rays are pushed upward, thus creating a negative current upward, and all the rays projected downward from the upper sheet are stopped when this current is saturated.

The order of magnitude of the velocity of the secondary rays, supposing them to be electrons, may be estimated from the difference of potential required to stop them. If V is this difference of potential, and v, m, and e are the maximum vertical velocity, mass and charge of the electrons

$$\frac{1}{2} mv^2 = Ve$$

$$\text{or} \quad v = \sqrt{2\frac{Ve}{m}}$$

For electrons $\frac{e}{m} = 1{\cdot}77 \times 10^7$, and taking for V 40 volts $= 4 \times 10^9$ $e, m, u,$ we have

$$v = 3{\cdot}74 \times 10^8 \frac{\text{cm.}}{\text{sec.}}$$

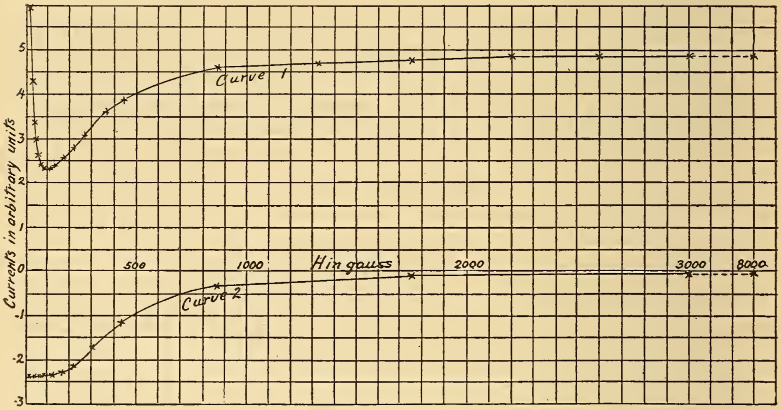
It must be borne in mind that those rays, to which the name β-ray has been attached, have velocities greater than $10^{10} \frac{\text{cm.}}{\text{sec.}}$, and that a difference of potential of many thousands of volts would be required to stop them. The α-rays could not be stopped by any difference of potential obtainable.

The general truth of the above manner of explaining the currents is confirmed by measurements with a magnetic field. On putting the cylinder B to earth and on increasing the magnetic field from 0 to 8000 gauss, one observes the currents represented by curve 1 in figure 3. Up to about 60 gauss there is a sharp fall in the value of the current. That this is due to the suppression of the secondary rays by the magnetic field may be made clear by the following considerations: The effect produced by the magnetic field H on the secondary rays is to make them move along the surfaces of circular cylinders, whose axes lie in the direction of the magnetic force, and whose radii r are given by the well known formula

$$Hr = \frac{mv}{e}$$

Now none of the electrons starting from one sheet of aluminium can reach the other, if the maximum diameter of these cylinders corresponding to the maximum value of v is less than the smallest distance between the sheets. To allow for the bulging of the sheets this distance may be taken to be about $\cdot 8^{\mathrm{mm}}$. The maximum vertical velocity is $37 \cdot 4 \times 10^8$, and there is no reason for supposing that the horizontal velocity is any greater. Hence substituting $r = \cdot 4^{\mathrm{cm}}$ and $v = 3 \cdot 74 \times 10^8$, we have

FIG. 3.



$$H = 53 \text{ gauss}$$

This is not far from the value of the magnetic field at the end of the sharp fall in the currents represented by curve 1 (fig. 3), and we may conclude that the currents beyond the minimum valve of this curve are due to the α- and β-rays alone, the secondary rays having been suppressed.

Curve 2 (figure 3) represents currents measured with a sheet of aluminium $\cdot 048^{\mathrm{mm}}$ thick covering the hole C. This sheet stops the α-rays but lets most of the β-rays through, and it is interesting to note that there is no initial drop in the curve, indicating that the β-rays do not produce secondary rays of small velocity.

The above results are similar to and confirm results obtained several years ago* in experiments on the secondary rays due to the α-rays from radium itself and from radium C.

The curves in figure 3 indicate an increase in the current, starting from field strengths of about 115 gauss, until a maximum value is reached in the neighborhood of 3000 gauss. The increase is due to the progressive suppression of the β-rays by the magnetic field, and the maximum represents the charge carried by the α-rays alone.

The smallest velocity of the β-rays may be estimated by the formula of Lorentz

$$\mathrm{H}r = \frac{mw}{e}\,\frac{\mu}{\sqrt{1-\mu^2}}$$

where μ is the ratio of the velocity v of the β-particle to the velocity w of light. We have seen above that a ray will not be stopped by the field, if the radius of curvature of its path is greater than 10^{cm}; and since a field of 115 gauss begins to stop the β-rays, the value of Hr for the slowest of them is 1150, corresponding to a velocity of about $1{\cdot}7\times10^{10}$. This value is of the same order of magnitude as that ($1{\cdot}85\times10^{10}$) of the slowest beams of rays previously observed coming from a thin-walled glass tube containing radium emanation,† and we conclude that there are no β-rays from our source stopped by fields smaller than that corresponding to the minimum of curve 1 (figure 3).

On account of the flatness of the curves the maximum velocity of the β-rays is difficult to estimate. Those that are just suppressed by a field of 2500 gauss have a velocity of about 98 per cent of that of light, and 5000 gauss is sufficient to stop the fastest β-rays the velocity of which has been measured.

We assume, therefore, that the current observed with a field of 8000 gauss corresponds to the charge carried by the α-rays alone, and that the minimum corresponds to the α-ray charge diminished by that of all the β-rays capable of penetrating the glass of these thin spheres.

Messrs. Hahn and v. Baeyer and Miss Meitner have observed a few rays slower than the above, which they attribute to radium B. These rays, however, probably do not get out of the little sphere and are not measured in these experiments.

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* Duane: Science, xxiv, 48, 49, 1906; Le Radium, February, 1908; Comptes rendus, July, 1908.

† Danysz, Le Radium, 1911.

A number of measurements have been made to ascertain the effect produced by superposing electric fields on the magnetic field. In general, if the magnetic field is small, the electric field produces a large change in the value of the currents. Charging the cylinder B to +88 volts, for instance, increases the current to four or five times its value, while, if the potential is −88 volts, the current is diminished about the same amount, becoming negative. These changes are due, undoubtedly, to the drift produced by the electric field in the electrons forming the secondary rays, in spite of the suppressing effect of the magnetic field.

On the other hand, the saturated current for large magnetic fields is not changed more than a few per cent (1−8) by electric fields up to 1800 volts. In general, the effect due to a positive charge given to the cylinder B is somewhat greater than that due to a negative charge. The effect of small electric fields is small; for instance, in one experiment with H = 8000 gauss, an electric field of +2 volts increased the current 2·5 per cent, and a field of −2 volts decreased it ·8 per cent, When the cylinder B is put to earth the electric field is very small, for both B and E are covered with sheets of the same metal, aluminium, and we are safe in assuming that the maximum current is not altered appreciably by any small drift in the electrons due to the Volta electromotive force.

A number of experiments have been made to determine the magnitude of the charge carried by the α-rays from a given quantity of emanation. In a preliminary experiment, in which the glass sphere containing the emanation was small, the positive charge did not decrease with the time as fast as it should according to the law of decay of the emanation. This was probably due to a gradual shifting of the bubble of emanation in the sphere, portions of the latter's walls being too thick to allow all the α-particles to pass through.

This progressive change did not take place in the two series of experiments, the data of which is contained in the subjoined table. In these experiments the spheres had much larger volumes than the bubbles, and the currents followed very closely the law of decay of the emanation with the time.

The quantity of emanation contained in each of the glass spheres was measured by comparing the ionization due to its γ-rays with that due to the γ-rays from a secondary radium standard belonging to the laboratory of Madame Curie. This standard had been compared previously with the international primary standard. A correction was made for the difference in thickness of the glass of the little sphere and that of the tube in the radium standard, the magnitude of the correction being estimated by covering a little bulb with a sheet of alu-

Experiment I. July.						Experiment II. August.					
1 Day and hour	2 Thickness of sheet	3 Emanation in curies	4 + Charge per second	5 + Current per curie	6 Ratio ∓ charge	7 Day and hour	8 Thickness of sheet	9 Emanation in curies	10 + Charge per second	11 + Current per curie	12 Ratio ∓ charge
	mm.						mm.				
20–22	nothing	·0623	·0217	·349	·53	3–17	beaten	·0465	·0178	·383	·65
20–24	nothing	·0604	·0215	·356	·54	3–22½	·004	·0446	·0167	·374	·66
21–10	nothing	·0562	·0207	·369	·54	4–10	·004	·0409	·0148	·362	·66
22–18	beaten	·0441	·0163	·370	·63	4–18	nothing	·0386	·0136	·352	·57
23–10	beaten	·0391	·0142	·364	·64	5–11½	nothing	·0338	·0120	·355	·54
23–14½	nothing	·0379	·0138	·364	·60	5–20	·004	·0317	·0119	·375	·69
23–16	·004	·0365	·0134	·367	·60	6–17½	·004	·0269	·0100	·372	·67
24–14½	·004	·0314	·0112	·357	·67	6–22½	beaten	·0259	·00980	·374	·70
24–16½	nothing	·0311	·0112	·360	·61	7–11½	beaten	·0237	·00870	·367	·68
25–10	nothing	·0273	·00985	·361	·58	7–18	beaten	·0223	·00795	·358	·67
25–16	·004	·0261	·00945	·362	·71	8–11½	beaten	·0198	·00685	·346	·66
25–18	·004	·0257	·00935	·364	·73	8–18	beaten	·0188	·00660	·351	·63
26– 0	beaten	·0246	·00860	·350	·63	9–14½	beaten	·0161	·00605	·378	·65
26–10	beaten	·0228	·00795	·349	·60	10–11½	beaten	·0137	·00525	·383	·66

minium equivalent in thickness to the walls of the radium standard tube. The figures in columns 3 and 9 represent the quantities of emanation in the spheres at the time of the experiments (columns 1 and 7), and were calculated by means of the law of decay of the emanation, using the constant $\lambda = \cdot 0075$ (hour^{-1}). The quantities of emanation are expressed in curies, the curie being the amount of emanation in equilibrium with one gram of radium.

Columns 4 and 10 contain the observed charges in electrostatic units received per second by the box E, with a magnetic field of 8000 gauss and the cylinder B put to earth; and columns 5 and 11 contain the values of these charges divided by the corresponding quantities of emanation, that is, the charges per second due to the *α*-rays from one curie of emanation.

That all the *α*-rays projected vertically upward emerge from the glass sphere in these experiments may be inferred as follows: columns 2 and 8 contain the thicknesses of the sheets of aluminium that covered the hole C, and it appears that a sheet $\cdot 004^{\text{mm}}$ thick did not diminish the magnitude of the current per curie of emanation. All the *α*-particles, therefore, must have left the surface of the glass with at least a certain minimum velocity. The magnitude of this minimum velocity may be estimated from the fact that no diminution in the charge measured occurred on increasing the magnetic field up to 8000 gauss. We have seen that, if rays are not stopped by the field the radii of their paths must be at least 10^{cm}. Hence, for the *α*-rays from the sphere

$$\text{H}r = \frac{mv}{e} > 80000$$

or since, $\frac{e}{m} = 5 \times 10^3$ approximately,

$$v > 4 \times 10^8 \, \frac{\text{cm.}}{\text{sec.}}$$

The velocity of the *α*-particle when projected from the emanation is 17×10^8, and therefore all the *α*-particles emerging from the sphere must have had velocities greater than about a quarter of this. It follows that all the *α*-particles projected upward must have passed through the glass wall of the sphere, for, if a part of this wall had stopped *α*-particles neighboring portions would have just let them through, and these would have had small velocities.*

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* A diminution of the maximum current due to increasing the field up to 8000 gauss was observed in the preliminary experiment mentioned above.

For the same reason there cannot have been a diffusion of the atoms of radium A, B, or C into the mercury a sufficient distance to appreciably absorb the α-rays.

The average value of the charge per curie is ·363 e. s. u. per second, and since, as we have seen, only ·00400 of the rays projected in all directions pass through the hole C, the total charge carried by all the α-rays from one curie of emanation with the equilibrium amounts of radium A B C is 90·8 e. s. u. per second. This is almost three times the charge 31·6 carried per second by the α-rays from radium C alone, as measured by Rutherford and Geiger,* and corresponds to three times as many α-particles, those from the emanation and radium A as well as radium C.

It is well known that a number of important constants can be calculated from the value of the charge carried by the α-rays. Among them the following may be determined by using accurately known data only:

In the first place we may calculate the volume v of helium produced per second by one gram of radium together with its emanation and radium A B C, using simply the volume of hydrogen liberated in the electrolysis of water. One ampere liberates ·123$^{\mathrm{cm}^3}$ of hydrogen per second at 15°, and therefore if N is the number of molecules in 1$^{\mathrm{cm}^3}$ at 15° and e is the elementary charge in e. s. u.

$$Ne = 1{\cdot}22 \times 10^{10}$$

Since each α-particle carries the charge $2e$ the total charge carried by the α-particles from the gram of radium is $2vNe$ per second. Remembering to add the α-particle from the radium itself to those from the emanation and radium A and C we have

$$2Nev = \frac{4}{3} \times 90{\cdot}8$$

$$\text{or} \quad v = 4{\cdot}96 \times 10^{-9} \frac{\mathrm{cm}^3.}{\mathrm{sec.}}$$

This gives for the volume of helium produced per year per gram of radium 157$^{\mathrm{mm}^3}$ at 15°. Boltwood and Rutherford† recently found 156$^{\mathrm{mm}^3}$ at 0°.

The volume V of the emanation in equilibrium with one gram of radium may be calculated by using in addition to the above data the constants λ of the emanation, which has been very accurately measured,‡ and is $\lambda = 2{\cdot}085 \times 10^{-6}$ (sec^{-1}).

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* Royal Society Proc., A., Aug. 27, 1908.

† Sitzungsber. Akad. Wiss., Wien, March, 1912.

‡ Madame Curie, Traité de Radioactivité, I, chap. vi. Rutherford, Sitzungsber. Akad. Wiss., Wien, March, 1912.

Assuming that each atom of emanation that disintegrates produces one atom of helium, it appears that the volume of helium produced per second by the emanation alone (i. e. $\frac{1}{4}v$) must equal the volume of emanation that disappears per second, and this from the definition of λ is λV. Hence

$$\tfrac{1}{4}v = \lambda V = 1{\cdot}24 \times 10^{-9}$$
$$\text{and} \quad V = {\cdot}594^{\text{mm}} \text{ at } 15^\circ$$

The average of the best measurements of this volume is 60^{mm^3},* the measurements themselves varying between $\cdot 52^{\text{mm}^3}$ and $\cdot 66^{\text{mm}^3}$.

The constant of radium itself can be calculated from the volume of helium ($\frac{1}{4}v$) produced per second from one gram, and from the atomic weight of radium 226 : for, assuming that one atom of radium on disintegrating produces one atom of helium, $\frac{1}{4}v$ represents the volume that would be occupied by the fraction of a gram of radium disintegrating per second, if it were a gas. The mass of this fraction equals $\frac{1}{4}v$ multiplied by 226 and by one-half the mass of a cubic centimeter of hydrogen, and also equals by definition the constant λ' of radium. Hence

$$\lambda' = 1{\cdot}26 \times 10^{-11} \text{ (sec}^{-1}\text{)}.$$

This corresponds to the disintegration of half a given mass of radium in 1800 years.

In making the above calculations we have followed the generally accepted theory of radio-active transformations, assuming that each atom that disintegrates, except those of radium B, emits a single atom of helium carrying a double charge. The only data used in addition to the charge carried by the α-rays from a given quantity of emanation are such well known constants as the mass of a cm^3 of hydrogen, the volume of hydrogen liberated per second by one ampere of current, the constant of the emanation and the atomic weight of radium. The actual number N of molecules per cm^3 of gas and the magnitude of the elementary charge do not enter separately into the calculations. We may obtain a value of the elementary charge, however, by taking the number of α-particles expelled per second by the quantity of radium C in equilibrium with one gram of radium determined by Rutherford and Geiger.† This number is $n = 3{\cdot}4 \times 10^{-10}$, from which we have

$$e = 4{\cdot}46 \times 10^{-10} \text{ } e.\ s.\ u.$$

This is several per cent smaller than some of the best values recently published, and if we take $4{\cdot}7 \times 10^{-10}$ as a good average of these values of e, we get for n

$$n = 3{\cdot}22 \times 10^{10}$$

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* Rutherford, Phil. Mag., 1908; Debierne, Comptes rendus, May, 1909; Ramsay and Gray, Chem. Soc., 1909.

† Roy. Soc. Proc., A, lxxxi, Aug. 27, 1908; Phys. Zeitschr., 1909.

as the number of α-particles emitted per second by one gram of radium alone.

Columns 6 and 12 in the table contain the ratios of the negative to the positive charges projected vertically upward from the little spheres. The negative charge was estimated by taking the difference between the minimum and the saturated values of the currents, the former for field strengths of about 80 gauss, and the latter, 8000 gauss. The average value of the ratio is ·63, and, assuming that a β-particle carries half the charge of an α-particle, this corresponds to the emission in the vertical direction of 3·8 β-particles for every three α-particles.

It must be borne in mind that some of the β-particles come from the surface of the mercury in the little spheres either by reflection or as secondary rays. A rough estimate of the number of β-particles due to this effect may be obtained from the following experiment. A very small thin-walled sphere of glass was filled with emanation, but no mercury was allowed to flow into it. On measuring the charges with this sphere as the source of rays the following ratios were found :

Charge ∓ ·52, ·535, ·52, ·485, ·485, ·48 ; average ·505

which corresponds to three β-particles for every three α-particles. In this experiment there was no metal in the immediate neighborhood of the sphere. On placing a small sheet of brass about 1^{mm} thick close under the sphere, however, the ratio was found to increase, the values being

Charge ∓ ·605, ·615, ·625, ·61 ; average ·615.

This is approximately the ratio obtained with mercury in the sphere.

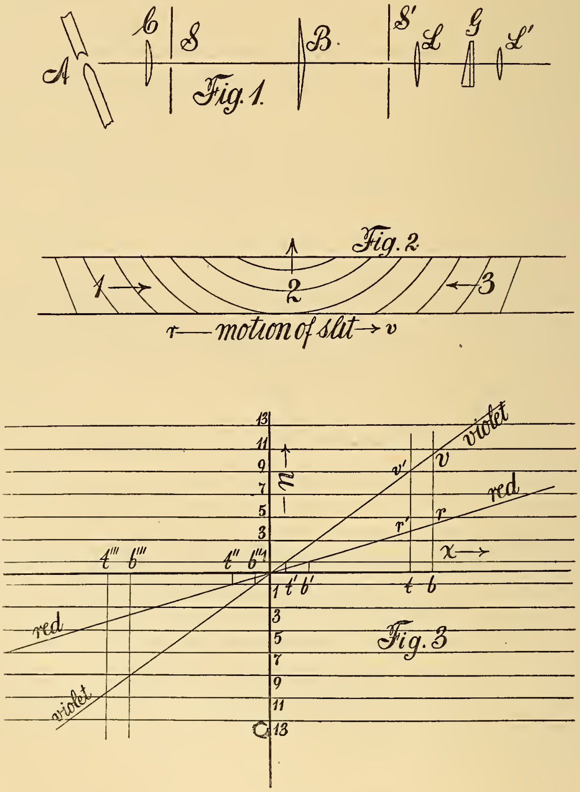
From these experiments we conclude that the number of β-particles emitted by the emanation and radium A B C, and capable of traversing the thin walls of the spheres, is about equal to the number of α-particles emitted in the same length of time.* To get the total number of β-particles actually projected from the active substances we must add to the above those few slow β-particles that are known to come from radium B with perhaps other slow ones that may be emitted by the emanation and radium A.

* Rutherford, Phil. Mag. 1905 ; Makower, Phil. Mag. 1909.

Art. XXVII.—*The Resolution of Interference Fringes;* by C. Barus.

1. *Experiment.*—The following remarks apply to interference fringes produced preferably by the bi-prism, though Young's slits and the other methods of course show the same results. The experiment is straightforward, as is given in fig. 1, but the effect obtained is at first quite unexpected.

Figs. 1, 2, 3.



In fig. 1 the arc light *A* passing the condenser *C* and the slit *S*, falls on the bi-prism *B* and then upon the direct vision spectroscope *S′ G* (preferably of the grating form like that of Mr. Ives), where *S′* is the slit, *G* the grating with attached prism, *L* and *L′* the collimator and eyepiece, respectively. Both slits *S* and *S′* must be as fine as possible, the spectrum seen being just short of darkness to obtain the sharpest effects, though the results are perfectly distinct, if more washed, for wider slits.

What one would expect to see as the spectroscope $S'G$ is moved across the field from left to right is the usual form of channeled spectrum, with the fringes moving horizontally from end to end of it. What actually appears, however, is a succession of intercepts between an upper and a lower horizontal, of broad concentrically circular or oval absorption bands, all of a very large radius, the displacement being on the plan shown in fig. 2, or the reverse. In other words, the spectroscope reveals the similarly intercepted arcs of large absorption bands. The arcs if essentially horizontal move up and down, if essentially vertical right and left. They are never quite vertical, and they become thinner and more crowded toward the ends of the spectrum. The groups 1, 2, 3, appear in succession.

The phenomenon is exceptionally sensitive to changes in the approximate verticality of the slit, so that if the spectroscope is slightly rotated on its axis, all the groups may reappear in turn.

2. *Explanation.*—To interpret this phenomenon it is convenient to plot the order n of a given fringe in terms of its distance x from the center of fringes, where $n = (c / r(\lambda / 2))x$, r being the virtual distance of the fringes on the screen, here the slit of the spectroscope, from the virtual position of the two slit images for the wave length λ. There will be dark bands for a given color λ, as fig. 3 shows, whenever $n = 1, 3, 5$, etc. The two lines drawn show the limits of the spectrum for any distance of fringe x and the heavy horizontal lines the number of dark bands to be expected. Thus for the value of x corresponding to vr, there will be three black bands in the spectrum, their color distribution depending upon their position between v and r. As the slit moves from right to left from the positive to the negative values of x, bands will enter the red end and leave the violet end, for a positive value of x and do just the reverse for a negative value of x.

The question now arises as to what will happen if the fine slit is not quite parallel to the fine interference fringes, crowded together as they are in a vertical band about half an inch in breadth. The oblique but fine slit in such a case corresponds to a succession of values of x depending upon the obliquity and length of the slit, and the diagram, fig. 3, therefore, shows the case for only one point in the length of the slit. It is thus necessary to introduce the third dimension corresponding to the breadth of spectrum, at right angles to the plane of fig. 3, which plane may be supposed to correspond to the bottom point of the slit. If the horizontal projection of the oblique line of the effective slit is tb, the spectrum corresponding to the top point of the slit will be $v'r'$, so that all the bands have been displaced toward the violet. Since the internal points of the slit correspond to the intermediate spectra between vr and $v'r'$, the spectrum will thus contain curved black bands with the tops toward the violet and their bottom toward the red. Precisely the opposite will be the case at $t'''b'''$ for a negative value of x, *i.e.*, on the other side of the center of interference fringes. If the slit moves, the general motion of bands will remain as already explained, only there must now be successive changes of form.

Thus if the slit takes the position $t'b'$ (some distance apart from top to bottom of spectrum) there can be but one black band in the spectrum, running from the red at the bottom to the violet at the top and being, therefore, nearly horizontal. At $t''b''$ a single band must run from the violet at the bottom to the red at the top, *i. e.*, with reversed slope, so that clearly with the projected slit symmetrical to $x=0$ the bands if appearing (as they do in multiple in a proper position of the bi-prism B, fig. 1, close to the spectroscope $S'G$), must be quite horizontal in the middle and curved upwards, or the reverse, at both ends.

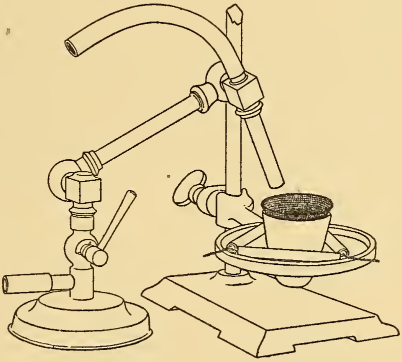
Following fig. 3 for a given obliquity and length of slit, all conditions may be easily computed. It is clear, moreover, that the bands can never be closed curves, but are limited to arcs cut off by the band of spectrum from a series of concentric closed curves. In this respect they differ from the elliptic interferences, which they in many respects recall; but the elliptics are essentially closed curves moving as a whole in the same direction.

Brown University, Providence, R. I.

ART. XXVIII.—*The Purification of Barium Sulphate precipitated in the Determination of Barium*; by F. A. GOOCH and D. U. HILL.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxlii.]

WHEN in the determination of barium as the sulphate the precipitation is made in the presence of alkali salts, considerable errors—sometimes as much as 20 milligrams in one half gram of precipitate—may be occasioned by occlusion of the foreign salts. It has been found that, upon dissolving the precipitate of barium sulphate in concentrated sulphuric acid and evaporating to dryness, the barium sulphate crystallizes in more or less coarsely granular crystals which may be washed free from the other sulphates.* The evaporation must be made with special care in order to avoid loss by spattering and creeping. With a ring burner this process takes several hours, but with a Hempel burner an evaporation can be made safely in about one half hour. The present object has been to find out whether the evaporation cannot be safely made by directing the flame of a blast lamp down upon the surface of the liquid, thus substituting for the Hempel burner a piece of apparatus that is in more general use.



Preliminary experiments to determine whether an evaporation without loss of barium sulphate could be made with the blast lamp were carried out in the following manner: Crystallized barium chloride (C.P.) was powdered and bottled without drying, and the water content determined by gentle ignition. Of this salt portions of 0·5000 grm. each were weighed into a previously weighed platinum crucible. About 5$^{cm^3}$ of water

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* Mar, this Journal, xli, 295, 1891.

was added, and then from 2^{cm^3} to 5^{cm^3} of sulphuric acid. The water and excess of sulphuric acid were evaporated off by directing a small flame from the blast lamp nearly vertically downward upon the liquid. The evaporation required about fifteen minutes. The results obtained upon weighing the crucible and barium sulphate were satisfactory in three cases out of five, but in the other two cases there was loss. To prevent this a cone of fine platinum gauze was fitted into the mouth of the crucible and the flame was directed against the point of the cone. This prevented the loss by spattering. The point of the cone must not be allowed to dip into the liquid, for otherwise some of the barium sulphate will be left above the gauze and may be blown away. The gauze was weighed with the crucible and cover each time, so that if any of the barium sulphate should spatter against the gauze its weight would not be lost. The results where the gauze was used were more consistently satisfactory and we felt encouraged to carry on further experiments using the gauze, but not without it. The average time required for completing an evaporation in these and subsequent experiments where the gauze was used was about one half hour. Table I gives the results of the experiments in which the naked flame was directed upon the solution, Table II those of the experiments in which the gauze was interposed.

TABLE 1.

Wt. of $BaCl_2 . 2H_2O$ taken grm.	$BaSO_4$ found grm.	$BaSO_4$ by theory grm.	Error grm.
0·4996	0·4774	0·4773	+0·0001
0·4996	0·4774	0·4773	+0·0001
0·4996	0·4747	0·4773	—0·0026
0·4996	0·4773	0·4773	0·0000
0·4996	0·4765	0·4773	—0·0008

TABLE II.

Wt. of $BaCl_2 . 2H_2O$ taken grm.	$BaSO_4$ found grm.	$BaSO_4$ by theory grm.	Error grm.
0·4996	0·4770	0 4773	—0·0003*
0·4996	0·4777	0·4773	+0·0004
0·4996	0·4768	0·4773	—0·0005
0·4996	0·4768	0·4773	—0·0005
0·4996	0·4774	0·4773	+0·0001
0·4996	0·4776	0·4773	+0·0003

* The tip of the gauze dipped into the liquid.

For use in the subsequent experiments a solution to contain approximately 0·5 grm. of $BaCl_2 . 2H_2O$ in 50^{cm^3} was prepared by weighing out 20 grm. of the $BaCl_2 . 2H_2O$, transferring it to a 2-liter measuring flask, and filling the flask to the mark with distilled water. The quantity of the solution used in each experiment was determined by drawing portions of 50^{cm^3} from a burette into previously weighed glass-stoppered Erlenmeyer flasks and weighing. Since 0·01 grm. of the solution contained only 0·0001 grm. of $BaCl_3 . 2H_2O$, it was not necessary to weigh more accurately than to one centigram. However, the weighing was usually made to a milligram.

In the first series of experiments determinations of barium in the absence of salts of other metals were made in the usual manner, and the effect of the treatment of the precipitate of barium sulphate with sulphuric acid in the way described was tried. The procedure in detail was as follows: One cubic centimeter of strong sulphuric acid was added to 100^{cm^3} of water in a 250 or 350^{cm^3} beaker, and the mixture was heated to boiling. The weighed amount of barium chloride solution was washed from the Erlenmeyer flask into the hot acid solution. The beaker was then allowed to stand on the steam-bath for a few hours, and in most cases at least one night intervened between the precipitating and the filtering of the material. The precipitate was filtered on ashless paper (ash 0·00011 grm.) without using pressure, ignited with the paper in a weighed platinum crucible, and brought to constant weight with a Bunsen burner. From 2 to 5^{cm^3} of sulphuric acid were then added, the gauze cone fitted in the crucible, the evaporation made as in the previously described experiments, and the crucible with its contents, the gauze, and cover, weighed. Only a trifling change of weight would be expected, since the only solid material that could be occluded in the original precipitate is barium chloride. As this would take the place of an equivalent amount of the sulphate, and the molecular weights of the chloride and sulphate do not differ greatly, no very great error could be introduced in this way. In the reverse process—the determination of sulphate by precipitation with excess of barium chloride—"the occlusion of barium chloride in the precipitate of barium sulphate may lead to very serious error." * Table III gives the results of the experiments just described, corrected for the filter ash, 0·0001 grm.

In the next series of experiments, 10^{cm^3} portions of a 20 per cent solution of potassium chloride were added to the 100^{cm^3} of water and the 1^{cm^3} of sulphuric acid before the precipitation was made. The procedure just described was then followed to the point where the evaporation with sulphuric acid was completed. The material was then washed from the crucible

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* Richards and Parker, Proc. Amer. Acad. Sci., vol. xxxi, p. 76.

Table III.

			Results reduced to 50 grm. of solution			
Wt. of $BaCl_2$ sol. used grm.	$BaSO_4$ found before treatm't grm.	$BaSO_4$ found after treatm't grm.	$BaSO_4$ before treatm't grm.	$BaSO_4$ after treatm't grm.	$BaSO_4$ by theory grm.	Error grm.
50·281	0·4767	0·4766	0·4740	0·4739	0·4737	+0·0002
50·348	0·4784	0·4771	0·4751	0·4738	0·4737	+0·0001
50·199	0·4764	0·4754	0·4745	0·4735	0·4737	−0·0002
50·293	0·4786	0·4765	0·4758	0·4737	0·4737	0·0000

onto a filter-paper and washed thoroughly to remove the potassium sulphate. The filter was dried and ignited in the crucible, and the crucible and contents brought to constant weight. Table IV gives the results of this series. Correction has been made for the weight of the ash (0·0001 grm.) of the second filter-paper, that of the first paper having been dissolved, presumably, by the treatment with sulphuric acid.

Table IV.

			Results reduced to 50 grm. of solution.			
Wt. of $BaCl_2$ sol. used. grm	$BaSO_4$ found before treatm't grm.	$BaSO_4$ found after treatm't grm.	$BaSO_4$ before treatm't grm.	$BaSO_4$ after treatm't grm.	$BaSO_4$ by theory grm.	Error grm
50·262	0·4814	0·4749	0·4789	0·4724	0·4737	−0·0013
50·171	0·4870	0·4772	0·4854	0·4756	0·4737	+0·0019
50·281	0·4804	0·4759	0·4777	0·4732	0·4737	−0·0005
50·285	0·4838	0·4762	0·4810	0·4735	0·4737	−0·0002
50·330	0·4805	0·4755	0 4774	0·4724	0·4737	−0·0013
50·320	0·4818	0·4766	0·4787	0·4736	0·4737	−0·0001
50·278	0·4813	0·4765	0·4786	0·4738	0·4737	+0·0001
50·301	0·4804	0·4751	0·4775	0·4723	0·4737	−0·0014*
50·274	0·4797	0·4762	0·4771	0·4736	0·4737	−0·0001
50·235	0·4790	0·4753	0·4768	0·4731	0·4737	−0·0006
		Av.	0·4789	0·4733		

* A slight loss by creeping was expected in this experiment.

This investigation shows that the evaporation can be carried out successfully with the use of the blast lamp and platinum gauze as a substitute for the Hempel burner, and that, although the accuracy of the results is not as great as could be wished, yet, where alkali salts are present, this method of purification reduces the otherwise very large error to a value at most not more than one or two milligrams for half a gram of barium sulphate.

Art. XXIX.—*The Significance of the Piltdown Skull:* by George Grant MacCurdy.

A discovery of unusual importance from the viewpoint of human origins was officially announced on December 18 at a meeting of the Geological Society of London. Briefly the facts are these. Four years ago in passing up the Ouse valley from his home in Lewes (Sussex) into the Weald, Mr. Charles Dawson, Fellow of the Society of Antiquaries and of the Geological Society, noticed that the roadway had been mended recently with flints of a kind that he had not seen before in that region. These were traced to their source, which proved to be a pit near Piltdown Common. Visiting the pit he learned that the workmen had dug out a "thing like a cocoanut" and after breaking it up had thrown away the pieces. After a long search Mr. Dawson and Dr. A. Smith Woodward, of the Natural History Museum, London, recovered most of the fragments, which proved to be parts of a human skull. At a later date the right half of a lower jaw with first and second molars in situ was dug out of the undisturbed gravel. Both skull and jaw came from about four feet below the surface and not far apart, so that both probably belong to the same individual. The bones are mineralized and stained to a ruddy-brown color as are the sands and flints among which they were found.

The most diligent search has failed to reveal other parts of this human skeleton. But the finding of fossil animal remains in the same pit, both associated with rudely worked flints, makes Piltdown one of the most extraordinary prehistoric stations ever uncovered. The fossils include broken pieces of a Pliocene type of elephant (*Elephas meridionalis*), a cusp of the molar of a mastodon, teeth of *Hippopotamus*, *Castor*, and *Equus*, and a fragment of an antler of *Cervus elaphus*. These were all in the same mineralized condition and of the same color as the human bones.

When the pieces of the cranium were all put together, it was possible to estimate the cranial capacity, which Dr. A. Smith Woodward gives as not less than 1070^{cc}. The bones are tough and hard, and the walls of the brain case exceedingly thick, the average thickness of the frontal and parietal being at least one centimeter. The face and the greater part of the brow ridge are missing. The length of the cranium from glabella to inion is about 190^{mm}, while the greatest parietal width is 150^{mm}. The forehead is steeper and the brow ridge feebler than in the later Neanderthal type. The cranium is low and broad with a marked flatness on top, and the mastoid processes are relatively small.

The lower jaw is, in some respects, more primitive than the cranium. The horizontal ramus is rather slender, resembling in shape that of a young chimpanzee, especially in the region of the symphysis. Only two teeth, the first and second molars, were found, and these were in their sockets. They are typically human although relatively of large size and narrow, thus requiring more linear space for their setting in the jaw. Each has a fifth cusp. The crowns are worn flat by mastication, indicating that the canines were not so prominent as to interfere with essentially human processes of trituration, also that the individual was of adult age. The ascending ramus is unusually broad and the sigmoid notch at the top in front of the articular process is shallow. In these respects, the Sussex lower jaw approaches that found near Heidelberg. The feeble

Fig. 1.

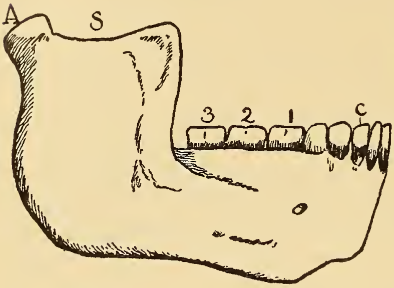

Fig. 2.

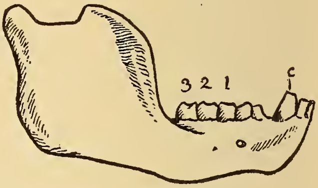

Fig. 3.

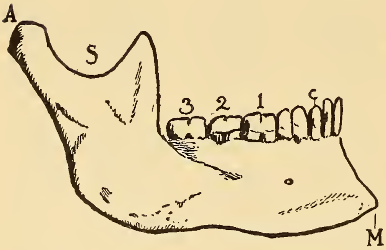

Fig. 4.

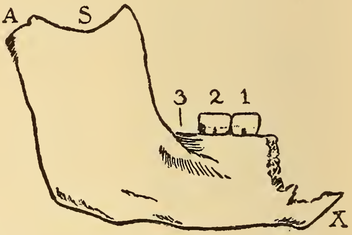

Fig. 1. Heidelberg man.
Fig. 3. Modern man.
Fig. 2. Chimpanzee.
Fig. 4. The Sussex jaw.

A, Articular process or condyle (broken in the Sussex lower jaw). S, Sigmoid notch. *c*, Canine tooth. 1, 2, 3, First, second, and third molars.
From a sketch by Sir Ray Lankester in *The Daily Telegraph.*

brow ridges, the small area for the insertion of the temporal muscles, the rather insignificant mastoid processes, and the slender lower jaw, point to a member of the female sex. Dr. Woodward regards the skull as belonging to a hitherto unknown species of *Homo*, for which he proposes the name *Eoanthropus dawsonii.*

A study of the cast of the cranial cavity would seem to justify this appellation. This has been done thoroughly by Professor G. Elliot Smith, one of the highest authorities on the human brain, who finds that while it bears a remarkable similarity to the brain cases of Gibraltar and La Quina, both paleolithic and supposedly feminine, the Piltdown brain case is smaller and more primitive in form than these. The most striking feature is the "pronounced gorilla-like drooping of the temporal region, due to the extreme narrowing of its posterior part, which causes a deep excavation of its under surface." This feeble development of that portion of the brain which is known to control the power of articulate speech is most significant. To Professor Smith the association of a simian jaw with a cranium more distinctly human is not surprising. The evolution of the human brain from the simian type involves a tripling of the superficial area of the cerebral cortex; and "this expansion was not like the mere growth of a muscle with exercise, but the gradual building-up of the most complex mechanism in existence. The growth of the brain preceded the refinement of the features and the somatic characters in general."

The associated worked flints have been compared with the so-called eoliths from the North and South Downs. According to Sir Ray Lankester, "many of the flints in this Piltdown gravel have been worked by early man into rough implements. They are of flat shape, often triangular in area, and show a coarse but unmistakable flaking of human workmanship." He considers them ruder and earlier than any flint implements that can be rightly called Chellean.

Scientists have often remarked on the paucity of human remains that could with certainty be referred to a very early epoch, a condition which more than anything else has kept in check the science of prehistoric anthropology. After all there is no evidence quite so incontrovertible as the presence of man's own skeletal remains. We may justly differ on the question as to whether or not a given flint is an artifact; not so in case of a human skull. When the skull is found associated with rudely flaked flints, the nature of which might be questioned if occurring alone, the burden of proof is at once shifted from those who believe them to have been utilized by man to those who would call them the work of Nature. On the other hand, this does not by any means let down the bars to indiscriminate claims for the artifact nature of all primitive looking flints. If a great majority of all the so-called eoliths or pre-Chellean types were thrown away, there would still be left enough to do business with as the case of Piltdown proves.

Personally I have for years been a believer in the prehistoric possibilities of southern England because of the outcrops of flint-bearing Chalk stretching from Dorset and Sussex on the south to Caddington and the Cromer Forest Beds on the north.* Of all raw materials flint is perhaps the best suited to tempt nascent *Homo* to become a tool-user. It is the most utilizable of all stones because of its hardness and mode of fracture, leaving a sharp straight edge. Flint flakes can be produced by purely natural means. The accidental stepping on one of these would suffice, after repetition at least, to prove their efficiency. Thus the oldest and most primitive implements that have come down to us are utilized flint chips. Once the flint-using habit was formed it spread; and when the natural supply became scarce it was supplemented by artificially produced chips. The chief sources of flint are the chalk deposits of Cretaceous age that occur so plentifully in western Europe—as seen for example in the white cliffs along the southern coast of England. Approaching one of these cliffs, you will find it studded with parallel beds of flint nodules. Wherever flint occurs stone-age relics are apt to be abundant.

It is not generally known to Channel voyagers that the white cliffs at Beachy Head and again more than 50 miles farther east at Dover are the bases of a great anticlinal fold whose axis passes from Dungeness in a westerly direction through Hampshire. The crest of the fold which once towered high over what is now the Weald disappeared ages ago, leaving two slender tongues from the great Chalk plain of Dorset, Wiltshire, and Hampshire, the tip of one (the North Downs) being at Dover, and that of the other (the South Downs) at Beachy Head. The scene of Dawson's epoch-making discovery is almost due north of Beachy Head just beyond the South Downs plateau and hence near the southern limits of the Weald. The Ouse takes its rise in the Weald, flows southward, cutting through the South Downs and emptying into the Channel at New Haven.

The Piltdown gravels are 80 feet higher than, and nearly a mile north, of the present stream-bed of the Ouse. This signifies a great age for the deposit. While it may not be so old as the patches of red clay with rude flints on the Downs north of Ightham as well as on the South Downs at Beachy Head and Eastbourne, some at least of the materials composing it

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* Amer. Anthropologist, vol. vii, 442, 1905.

may once have been a part of older deposits. The broken edges of all the bones, human as well as animal, were worn before finally coming to rest where they were found. The remains of the Pliocene elephant and *Mastodon* are most worn, but the difference in wear is not so marked as to exclude the possibility of all being coeval. All are as old as and may be older than the Piltdown gravel beds. They date as far back as the lower Quaternary and might even belong to the upper Pliocene. That rude implements of the eolithic type were associated with those human remains would seem to give to such implements a standing hitherto denied them by some authorities; unless it can be proved that they were derived from a deposit antedating that which originally contained the human remains. Their pedigree was needed in order to make industrial genealogy complete, just as the skull itself was needed to fill a missing gap in man's physical evolution. When the two sets of evidence are found intimately associated, they will serve as a solid basis for further advances in the domain of prehistoric anthropology. It remains for the geologists to determine whether in Piltdown the prehistorian's "Rosetta stone" has at last been found.

In the Smithsonian Report for 1909 (p. 581) I called attention to valley deposits as being the well-nigh inexhaustible storehouse of archeology; I was therefore prepared for such a striking confirmation as Piltdown affords. The one great drawback about valley deposit finds is that in the very nature of the case they must ever be in a large measure fortuitous. Cave deposits are so circumscribed that all one has to do is to find his cave and set his men to work. An expert can even afford to be on the spot almost continuously until the work is completed. On the other hand, untutored workmen are constantly digging in hundreds of sand, gravel, and clay pits over wide areas. Continuous expert control is out of the question without an international subsidy on a large scale. The result is that important data are overlooked and valuable specimens are smashed by pick and shovel and irretrievably lost to view. When by chance a find is made its authenticity is often open to grave question.

When the man of Sussex hunted in the valley of the Ouse was there an English Channel? The present Channel dates from the very close of the paleolithic. Raised beaches near Calais and on the south coast of England testify to the existence of an earlier channel, possibly during the Chellean epoch. At any rate the man of Sussex must have had neighbors to the south on what is now French soil. If there was no Channel the Ouse and the Somme were tributaries of the same large stream that flowed westward emptying into the Atlantic Ocean somewhere south of the Scilly Islands; and the same race would have made common hunting ground of this great valley system; for in a gravel terrace at Abbeville, d'Ault du Mesnil years ago found remains of practically the same fauna; and in a very old high-level gravel terrace at Amiens, Commont has noted the presence of a rude pre-Chellean flint industry akin to that at Piltdown. We may, therefore, reasonably expect to find in the Somme valley the osseous remains of this old race.

In Spain, at Torralba, near the crest of the Sierra Ministra east of Madrid, the Marquis of Cerralbo has recently uncovered a very ancient camp site that has yielded a pre-Chellean and Chellean industry mingled with the bones of possibly the same elephant, horse, and deer as were found at Piltdown. Both bones and implements occur so plentifully that the Marquis may yet be so fortunate as to turn out a human skull, for the site was not yet half exhausted on the occasion of my visit to Torralba last summer.

Twenty years elapsed between the finding of *Pithecanthropus* and *Eoanthropus*. During the intervening period only one discovery of human osseous remains approaching these in importance was made: the lower jaw from the Mauer sands near Heidelberg, found in 1907. It is too early to say just what ethnic relations existed among these three ancestral forms; whether they represent links in one chain or in separate chains. In point of age the Piltdown skull probably belongs to an intermediate stage. All three are older by far than *Homo neanderthalensis*, which in turn is older than the artistically inclined cave men who decorated their haunts with engravings and frescoes of their favorite game animals, the bison, horse, mammoth, and reindeer.

Mr. Dawson and his associates are to be commended for the exercise of a diligent patience worthy of Darwin himself. The first piece was found abont the time Schoetensack announced his discovery of the Heidelberg jaw. Mr. Dawson simply kept quiet and continued his search for more evidence. Years elapsed between the finding of two pieces that would fit together, and only last summer were enough found to meet the requirements set for themselves by the discoverer and Dr. Woodward. Thus have they quietly but none the less thoroughly built one more pier for the bridge that is to connect the present with the shores where the infancy of the race was cradled and its childhood played.

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *The Decomposition of Silicates.*—On account of the present high price of platinum, and the available means of attaining high temperatures, Walther Hempel recommends the use of barium carbonate for the analytical decomposition of silicates, a process proposed long ago by Deville. He states that the operation may be carried out in a platinum crucible of 5^{cc} capacity and 4 g. weight. For the ignition he uses a Hempel furnace heated by a gas blast-lamp in which a temperature of 1360° C. can be attained. Since Berzelius showed that silicates less basic than orthosilicates do not lose alkalies upon ignition, and since silicates as basic as this are easily decomposed by hydrochloric acid, the method is applicable to silicates containing alkalies, provided that not too great a proportion of barium carbonate is employed. With 1 g. of feldspar and 3 g. of barium carbonate the decomposition was complete after heating for 15 minutes at the temperature mentioned; the sintered mass was easily decomposed by dilute hydrochloric acid and the platinum crucible was not attacked. The same results were obtained with topaz and andalusite under the same conditions. The great advantage of the method consists in the fact that the barium is easily separated from the other metals by means of sulphuric acid.—*Zeitschr. f. analyt. Chem.*, lii, 86. H. L. W.

2. *The Presence of Manganese in Animals.*—Bertrand and Medigreceanu have examined many species of animals for manganese, and find that it is distributed without exception in the organism of all representatives of the animal kingdom. Among the vertebrates, the mammals contain the least of the metals, hardly more than a few hundredths of a milligram in 100 grams of the total organism, although proportions five or ten times as great occur among the birds, reptiles, batrachians and fishes. Among the invertebrates the amount of manganese is generally quite large, and it has been known previously that the mollusks contain comparatively large amounts of the metal. It appears, therefore, that the manganese plays an important part in the vital processes of all animals.—*Bulletin*, xiii, 18. H. L. W.

3. *A General Method for the Preparation of the Ammonium Salts of Organic Acids.*—The usual method of preparing these ammonium salts, which is by neutralizing the aqueous solution of an acid with ammonia and evaporating to crystallization, gives very unsatisfactory results owing to the hydrolytic action of water upon these salts, and the literature shows that comparatively few of them have been made and analyzed. Keiser and McMaster have now devised a method for this purpose which consists in dissolving the acid in ether or in a mixture of ether

and alcohol and passing a stream of dry ammonia gas into the solution. The ammonium salt is thus precipitated, usually in a crystalline condition. The authors have in this way prepared the ammonium salts of maleic, fumaric, mesaconic, citraconic, malonic and phthalic acids.—*Amer. Chem. Jour.*, xlix, 84.

H. L. W.

4. *The Behavior of Nitroglycerine when Heated.*—SNELLING and STORM, by the use of a special cabinet constructed of steel plates, with a window of very heavy plate glass, have been enabled to observe the effects of heating upon nitroglycerine in quantities of 2 or 3 grams. They have found that the substance begins to decompose at temperatures as low as 50 or 60° C., while at 70° C. the commercial product gives off appreciable quantities of nitrous acid in the course of 15 to 30 minutes. At these temperatures it is somewhat volatile, and as the temperature rises volatilization and decomposition increase. At 145° C. boiling occurs, which is due partly to decomposition and partly to volatilization. As the temperature increases the boiling becomes more violent and explosion takes place at about 218° C. After rapid decomposition has started the temperature tends to rise rapidly of its own accord on account of the heat given off by the decomposition. When the temperature is maintained at between 145 and 210° C., at atmospheric pressure, the nitroglycerine can be partly decomposed and partly distilled without a final explosion of the residue.—*Technical Paper 12, U. S. Bureau of Mines.*

H. L. W.

5. *An Illustration of the Luminosity of Phosphorus.*—A simple lecture experiment for showing this phenomenon has been described by D. F. TWISS. A vertical glass tube about an inch wide and 4 feet long is supplied at the bottom with a rubber stopper carrying a small glass tube which is bent upwards so as to be parallel to the large tube and of about the same height. A solution of phosphorus in olive oil is introduced into the larger tube so as to reach within about 6 inches of the top, and steady suction is applied at the mouth of this tube by means of a water pump. Air enters through the narrow tube and a beautiful series of bell-shaped phosphorescent air bubbles rises through the column of oil.—*Chem. News*, cvii, 16. H. L. W.

6. *Recent Advances in Organic Chemistry*; by A. W. STEWART. 8vo, pp. 320. London, 1911 (Longmans, Green and Co. Price $2.50 net).—This very useful book for more advanced students of the subject has now appeared in a new edition with many modifications to bring it up to date. Two new chapters have been added, one on quinoles, and another on the triphenylmethyl problem. The book is well written and affords very interesting and instructive reading. T. B. J.

7. *Review Questions and Problems in Chemistry*; by M. S. H. UNGER. 12mo, pp. 106. Boston, 1912 (Ginn and Company. Price 50c.).—This book has been prepared for use in reviewing the facts, theories, and laws of elementary chemistry. Many

problems are included. The questions and problems have been taken from the most recent examination papers and text-books. There is a great number of them, and a student who could answer them all correctly would certainly have a thorough knowledge of the subject. There are no explanations, and no answers are given. H. L. W.

8. *Spectrum of Ionium.*—The spectrum of a mixture of the pure oxides of ionium and thorium has been recently investigated by A. S. Russell and R. Rossi. The percentage of ionium oxide in the preparation can be calculated from the period of ionium taken in conjunction with the number of α-particles emitted by one gram of the substance per second. Soddy has found that, on certain assumptions, the period must be at least 100,000 years. Also, Geiger has found the above mentioned number of α-particles to be 10^8. From these data it follows that the per cent of ionium oxide in the mixture used cannot be less than 16.

The investigators photographed the arc spectrum of the mixture between the wave-lengths $\lambda=3800$ and $\lambda=5000$ Å. U. Two gratings were used successively, the one having a radius of curvature of about 3 feet, and the other about 21·5 feet. *Not a single new line was found,* although, under similar experimental conditions, the presence of one per cent of CeO_2 could be easily detected, and one per cent of U_3O_8 was just at the limit of detectability. A like negative result for the spectrum of ionium has also been found by Exner and Haschek, who investigated both the ultra-violet and visible regions of the spectrum.

The failure to obtain the lines of ionium may be explained on the ground that the period of ionium is much less than 100,000 years, as assumed above. In this event, at least one new radioactive body precedes ionium in the disintegration series between uranium X and radium. If such a substance exists it cannot emit α-rays (since all of these rays have been accounted for), but it may be either rayless or it may emit soft β-rays only. Hence, the percentage of ionium oxide present in the mixture may have been greatly overestimated; in other words, the amount of ionium in the preparation may have been too small to be detected spectroscopically under the experimental conditions. On the other hand, it is thinkable that ionium has no radiation in the region investigated or, possibly, ionium and thorium have identical spectra in the ultra-violet and visible portions of the spectrum. In any event, the question is still an open one, and the absence of a detectable spectrum is very interesting and suggestive.—*Proc. Roy. Soc.*, No. A, 598, p. 478. H. S. U.

9. *The Excitation of γ-Rays by α-Rays.*—The recent investigations of J. Chadwick have definitely established, for the first time, the fact that γ-rays may be excited when α-rays impinge on matter. The α-rays employed were emitted by radium emanation together with its active deposit. Since the radio-active material was sealed up in a glass tube with very thin walls special care had to be taken to avoid errors which might arise from the exci-

tation of γ-rays by the β-rays coming from the source, and also to show that the remaining γ-rays were in excess of the primary γ-radiation.

The method of experimenting may be briefly described as follows: The glass tube was first surrounded by some material of low atomic weight, such as aluminium. The whole was then enclosed in a tube composed of a metal of relatively high atomic weight, for example, gold. The ionization produced by the γ-rays coming from this system was next measured by the balance method of Rutherford and Chadwick. After this, the positions of the layers of aluminium and gold were interchanged so that the more dense metal was next to the glass tube and was bombarded by the α-rays. The ionization was again measured and it was found to be greater than in the first instance by about 1 part in 300 when the face of the ordinary ionization-chamber consisted of a sheet of aluminium 1^{mm} thick. In order to obtain more conclusive results a special form of air-tight ionization-chamber was constructed in such a manner as to readily admit of evacuation and subsequent filling with the saturated vapor either of carbon bisulphide or of methyl iodide. In this way the ionization produced by the excited γ-rays was increased relative to the ionization due to the primary γ-rays. In other words, advantage was taken of the difference in penetrating power of the γ-rays emitted by the radio-active material and the γ-rays excited by the α-particles. When carbon bisulphide was used, the ionization was about 5 per cent greater for the glass-gold-aluminium order than for the glass-aluminium-gold sequence. In the case of methyl iodide the difference was a little larger. By covering the glass tube with a sufficiently thick layer of aluminium foil to stop all the α-rays, and by showing experimentally that the ionization no longer altered its value when the aluminium and gold tubes were interchanged, it was demonstrated that the excess of γ-rays found in the previous experiments could not be due to the primary β-rays. The remaining possibilities were exhausted by employing a magnetic field in an obvious way to deflect the soft β-rays, etc.

Taking the ionization observed when the inner tube was aluminium as 100, the ionization obtained with gold as the inner tube was 104·8, with silver 102·5, with copper 101·2, and with paper 99·7. Consequently the excitation of γ-rays by α-rays has been thoroughly demonstrated. A brief account of further experiments by J. Chadwick and A. S. Russell is given in "Nature" for December 26, 1912. Due attention will be given to the results of the latest investigations as soon as they are published *in extenso*.—*Phil. Mag.*, January, 1913, p. 193. H. S. U.

10. *Direct Determination of the Mean Free Path of Gas Molecules.*—Up to the present time no direct method for the determination of the mean free path of uncharged gas molecules has been devised An ingenious solution of this problem has been worked out by J. Franck and G. Hertz. The key-note to the process consists in making measurements on the lengths of the

paths of gaseous *ions* which are constrained to pass through an uncharged gas, and by interpreting the data in terms of the mean free path of the molecules of the electrically neutral gas through which the ions are sent. In order to make the interpretation legitimate two conditions must be fulfilled. In the first place the experimental conditions must be so arranged as to prevent the ions from becoming complex by the process of "loading" with neutral molecules. The second condition requires the influence of the electric charge on the number of collisions, (that is, upon the free path), to be negligible. By measuring the *first* free path which an ion describes after its genesis the first condition is satisfied, for loading can only occur when an effective collision with a molecule takes place. Although the apparatus partially described below is so designed as to make the determination of the first uninterrupted ionic path possible, the investigators have made their method doubly sure by using pressures lying between $0{\cdot}03^{\text{mm}}$ and $0{\cdot}14^{\text{mm}}$ of mercury, since B. Todd has shown experimentally that complex ions are not formed at these pressures. Again, by employing ions of sufficiently high speed the influence of the charge on the mean free path of the neutral molecules can be made smaller than the remaining possible experimental errors.

The novelty of the apparatus consists essentially in using two parallel-plate condensers which are maintained accurately parallel to each other and which can be set at different distances apart. A small hole was made in the center of the top plate of the upper condenser and in this hole a small platinum spiral coated with aluminium phosphate was so adjusted as to be flush with the lower surface of the upper plate of the condenser. When the spiral was caused to glow by the passage through it of a suitable electric current, the coating became a sufficiently steady source of ions. The lower and movable condenser had a guard ring but no hole; otherwise it was exactly like the upper condenser, but inverted. The ions were first accelerated by a drop of 40 volts in descending through the upper condenser, then they continued uniformly through the space between the two condensers, and finally they were disposed of by the reverse field of 38 volts in the lower condenser. Denoting the distance between the condensers by x, it was shown that the familiar formula $N = N_0 e^{-\frac{x}{\lambda}}$ applied under the experimental conditions. The probable nature of the ions emitted by the spiral led the investigators to use hydrogen between the condensers. The mean free path, λ, was found to be $0{\cdot}157^{\text{mm}}$, corresponding to a pressure of 1^{mm} of mercury. Assuming $n_0 = 2{\cdot}80 \times {\cdot}10^{19}$, and also that the spiral emits "charged hydrogen molecules," the investigators deduce $\sigma = 2{\cdot}41 \times 10^{-8\,\text{cm}}$, where σ symbolizes the diameter of a molecule of hydrogen. This result agrees fairly well with the value $2{\cdot}17 \times 10^{-8\,\text{cm}}$ as calculated by Sutherland from the kinetic theory of uncharged gases and on the basis of quite different experimental data.— *Verh. d. Deutsch. Phys. Gesellsch.*, No. 11, 1912. H. S. U.

11. *Der energetische Imperativ;* by WILHELM OSTWALD. Pp. 544. Leipzig, 1912 (Akademische Verlagsgesellschaft m. b. H.).—Taken broadly, this volume is a philosophical treatment of all human affairs from the standpoint of energetics. The text is subdivided into five parts entitled respectively: (1) "Philosophie", (2) "Organisation und Internationalismus", (3) "Pazifismus", (4) "Unterrichtswesen", and (5) "Biographie". The author first proves that the second law of energetics is the ultimate and most general foundation of all phenomena of the will. This leads both to the recognition of the law of the dissipation of energy as the basis of all processes which Schopenhauer represents as manifestations of the primal will, and to an extension of the principle of economy of Mach. Ostwald then announces his discovery of a comprehensive generalization which "consists in the general application of the second law of energetics to the totality of events and in particular to the totality of human actions". From this follows the "Energetical Imperative" which the author formulates in the following maxim: "Don't squander energy, utilize it". ("Vergeude keine Energie, verwerte sie".) It is now doubtless clear how the last four subdivisions of the text afford fertile fields for the application of the preceding general principles.

The subject-matter is presented in a most interesting manner, and much food for thought may be found even in the sections which deal with such special problems as: universal language, universal monetary standard, pedantry of syllabication, the reading of numbers, improvement of the calendar, etc. It may be remarked, in conclusion, that the volume does not contain a preface. H. S. U.

12. *Abstract-Bulletin of the Physical Laboratory of the National Electric Lamp Association.* Vol. 1, No. 1, pp. viii, 127. Chicago, 1913 (Univ. of Chicago Press).—This laboratory was organized in Cleveland, Ohio, in the autumn of 1908 for the development of those branches of science with which the art of lighting is closely associated. Under the able guidance of the Director, Edward P. Hyde, sections in physics, physiology and psychology have been established. The first number of the bulletin contains abstracts of 28 different papers representing the original work of the laboratory from its inception to the summer of 1912. Since these abstracts have been carefully prepared by the authors of the original papers and since great care has been taken in the preparation of the diagrams and plates, the volume will be very acceptable to all who are interested in the special subjects presented. "Subsequent numbers of the *Abstract-Bulletin* will be issued as the further accumulation of published investigations may warrant." The work of this laboratory promises to be very fertile because the members of the staff are well-known investigators, some of whom have been connected with the National Bureau of Standards, in Washington. For example, the papers of Herbert E. Ives have already attracted the attention which their high quality justly deserves. H. S. U.

13. *A B C of Hydrodynamics;* by R. DE VILLAMIL. Pp. xi, 135, with 48 figures. London, 1912 (E. & F. N. Spon).—Concerning this book the author frankly says : "There is not very much that is new in it ; some of the quotations are so old that they have been forgotten, and so will appear to the reader of the ordinary text-books as if they were new. What is, I fancy, original is the way in which the matter is arranged and the subject presented". These statements are so modest as to be almost misleading, for the topics discussed are treated in such a clear, refreshing and common-sense manner as to give to the whole a high percentage of effective novelty. In other words, the text is very suggestive and it contains much wholesome food for thought, not only for students who are commencing the study of hydrodynamics but also for those who are thoroughly acquainted with the advanced mathematical treatises on the subject.

The text abounds in pertinent quotations from the writings of recognized authorities. At the end of each chapter a summary of the conclusions reached therein is given and a short list of "References" is appended. Although a few formulæ are quoted, the book can be profitably read with almost no knowledge of mathematics. A number of admirable experiments are suggested in the text and made clear by the associated diagrams. The index is preceded by a short appendix which touches upon the closely related subject of aerodynamics. H. S. U.

14. *Geometrical Optics;* by ARCHIBALD STANLEY PERCIVAL. Pp. vii, 132, with 59 figures. London, 1913 (Longmans, Green and Co.).—The author's object in publishing this volume is stated as follows: "This book is primarily intended for medical students as a text-book on the subject of Geometrical Optics for their preliminary scientific examinations, though it practically contains all the Optics required by an ophthalmic surgeon. It is hoped that it will also prove of service to students of physics, . . ." A fair idea of the scope of the text may be obtained from the titles of the chapters, which are : "I Illumination—Pinholes—Shadows, II Reflection at Plane Surfaces, III Reflection at a Spherical Surface, IV Refraction at Plane Surfaces, V Refraction at a Spherical Surface," and "VI Lenses." The explanations are very clear and as simple as possible. The proofs of the formulæ are sufficiently rigorous, and special emphasis is laid on the consistent and general use of algebraic signs. A few "questions" are asked at the end of each chapter and the answers are given just before the index. Also, a number of illustrative "examples" are formally stated, and the solutions worked out, in the text. The appendix treats of certain problems which are more difficult or intricate than the ones given in the preceding chapters. A useful feature of the book consists in the collection of formulæ which follows the appendix.

Having thus far called attention only to the merits of the volume in question, it now seems fair to point out two significant slips which the author has made. In the fine print, on page 42, originality for the convention of signs is claimed. This convention is not new, for it is used by such authorities as Czapski (1893), Kayser (1900), Southall (1910), etc. Again, on page 41, we find the following remarkable definition of a principal section of a prism, namely : "The median vertical plane that bisects the apical angle is called the principal plane, . . ." H. S. U.

15. *An Introduction to Mathematical Physics;* by R. A. HOUSTON. Pp. ix, 199, London, 1912 (Longmans, Green and Co.) —To the study of this book the student is supposed to bring a thorough knowledge of the calculus and a rather extensive acquaintance with the phenomena of physics. A considerable familiarity with dynamics is also presupposed. The first chapter is devoted to the subject of attraction, (gravitational and electrostatic), and covers the discussion of the fields due to lines, planes, spheres, cylinders, and ellipsoids, by the usual methods. The second chapter covers a considerable portion of classical hydrodynamics ; and the third, of Fourier series and heat conduction. In the fourth chapter on wave motion the various types of waves in strings and rods are considered in some detail and much attention is given to water waves. The fifth chapter is on electromagnetic theory and the major portion of it is devoted to electric waves and light. The last chapter is on thermodynamics, and covers the usual classical theory with applications to ideal gases.

It is obvious from the above summary that there is an immense amount of ground covered in the short space of two hundred pages. In order to accomplish this the author has had in almost every instance to sacrifice the physical to the mathematical discussion of the various topics. The book is however clearly and logically written and should form a valuable work of reference for advanced students. L. P. W.

16. *Practical Measurements in Radio-Activity;* by W. MAKOWER and H. GEIGER. Pp. 151, London, 1912 (Longmans, Green and Co.).—In an experimental science it is always advantageous when a precise and detailed description of the customary technical procedure and methods is available for the instruction of those without previous experience who desire to carry out practical work in the subject. The book at hand fulfils these requirements in a thoroughly satisfactory manner and supplies, in a very systematic manner, much valuable information not to be obtained from other sources. The construction, principles and adjustments of electrometers and electroscopes are first discussed in a comprehensive manner, the various types of radiation emitted by radio-active bodies and the methods by which they are identified and measured are next considered, while succeeding chapters on the active deposits and radio-active recoil, radio-active transformations, standard measurements, and the separation of radio-active substances supply a large amount of important data in connection with these branches of the subject. The book marks a very distinct advance over anything of a simi-

lar nature that has previously appeared, and is a valuable and important contribution to the practical side of radio-activity.

B. B. B.

17. *The Physical Review and the American Physical Society.*—In July-August, 1893, the *Physical Review* was started under the auspices of the physical department of Cornell University, and for nearly twenty years it has maintained a high standard and done an important work for the development of physics in this country. With the current number (for January, 1913, recently issued) the control of the Review has been transferred to the American Physical Society; a wider scope and greater usefulness thus seems assured to it.

II. GEOLOGY AND NATURAL HISTORY.

1. *Publications of the United States Geological Survey*; GEORGE OTIS SMITH, Director.—Recent publications of the U. S. Geological Survey are noted in the following list (continued from vol. xxxiv, p. 484):

FOLIO NO. 183.—Description of the Llano and Burnet Quadrangles; by SIDNEY PAIGE. Pp. 16; 6 figures, 3 colored maps, 11 plates.

MONOGRAPH.—Volume LI, Cambrian Brachiopoda; by CHARLES D. WALCOTT. Part I, Text. Pp. 872. Part II, Plates. Pp. 363; 104 plates. See p. 331.

PROFESSIONAL PAPER NO. 71.—Index to the Stratigraphy of North America; by BAILEY WILLIS. Compiled by the U. S. Geol. Survey in coöperation with the Geol. Survey of Canada and the Instituto Geológico de México under the supervision of BAILEY WILLIS and GEORGE W. STOSE. Pp. 894; one plate, 19 figures, and 5 inserts. Also under separate cover Geologic Map of North America.— See p. 195.

MINERAL RESOURCES of the United States, Calendar Year 1911. Part II. Nonmetals. Pp. 1224; 9 plates, 14 figures. The numerous separate chapters, already given to the public, are published together in this massive volume; the various fuels, clay products, building stones and other substances, not metallic, are included here.

Advance chapters giving the production of the various metals have also been issued; also a Summary of the Mineral Production of the United States in 1911 compiled by W. T. THOM. The usual large sheet, now published, gives in detail the quantity and value of Mineral Products for the years 1902 to 1911; this has been prepared by EDWARD W. PARKER, statistician in charge. The total value for all products in 1911 was nearly $1,920,000,000; this is less than the amount for 1910 by $72,000,000, which is explained almost entirely by a decrease in pig iron.

BULLETINS.—No. 471. Contributions to Economic Geology, 1910. Part II. Mineral Fuels. MARIUS R. CAMPBELL, Geologist-in-charge. Pp. 663; 62 plates, 15 figures.

No. 513. Pliocene and Pleistocene Foraminifera from Southern California; by RUFUS MATHER BAGG, JR. Pp. 153; 28 plates, 3 figures.

No. 515, 518. Results of Spirit Leveling; R. B. MARSHALL, Chief Geographer. Work done in Coöperation with the States. No. 515, Pennsylvania, 1899–1911. Pp. 164; 1 plate. No. 518. Ohio, 1911. Pp. 108; 1 plate.

No. 521. The Commercial Marbles of Western Vermont; by T. NELSON DALE. Pp. 170; 17 plates, 25 figures.

No. 523. Nitrate Deposits; by HOYT S. GALE. Pp. 36, 2 plates, 2 figures.

No. 524. Bibliography of North American Geology for 1911, with subject index; by JOHN M. NICKLES. Pp. 162.

WATER–SUPPLY PAPERS.—Surface Water Supply of the United States. Nos. 281, 283, 284, 289, 290 for 1910; 301, 304 for 1911. Prepared under the direction of M. O. LEIGHTON. No. 281. Part I. North Atlantic Coast; by C. C. BABB, C. C. COVERT, and R. H. BOLSTER. Pp. 305; 2 plates. No. 383. Part III. Ohio River Basin; by A. H. HORTON, M. R. HALL, and H. J. JACKSON. Pp. 158; 2 plates. No. 284. Part IV. St. Lawrence River Basin; by C. C. COVERT, A. H. HORTON, and R. H. BOLSTER. Pp. 125; 2 plates. No. 289. Part IX. Colorado River Basin; by W. B. FREEMAN, E. C. LA RUE, and H. D. PADGETT. Pp. 233; 4 plates. No. 290. Part X. The Great Basin; by E. C. LA RUE, F. F. HENSHAW, and E. A. PORTER. Pp. 26. No. 301. Part I, 1911. North Atlantic Coast; by C. C. BABB, C. C. COVERT, and R. H. BOLSTER. Pp. 221; 4 plates. No. 304, 1911. Part IV. St. Lawrence River Basin; by C. C. COVERT and R. H. BOLSTER. Pp. 98; 4 plates.

No. 293. Underground Water Resources of Iowa; by W. H. NORTON, W. S. HENDRIXSON, H. E. SIMPSON, O. E. MEINZER and others. Prepared in coöperation with the Iowa Geol. Survey. Pp. 994; 18 plates (2 in pocket), 6 figures.

No. 294. An Intensive Study of the Water Resources of a part of Owens Valley, California; by CHARLES H. LEE. Pp. 135; 30 plates, 8 figures.

Nos. 298, 299. Water Resources of California, prepared under the direction of JOHN C. HOYT. No. 298. Part I. Stream Measurements in Sacramento River Basin; by H. D. MCGLASHAN and F. F. HENSHAW. Pp. 411, with 8 plates and 3 figures.

No. 299. Part II. Same in San Joaquin River Basin; by H. D. MCGLASHAN and H. J. DEAN. Pp. 439; 7 plates.

2. *Second Annual Report of the Director of the Bureau of Mines*, JOSEPH A. HOLMES, *to the Secretary of the Interior*, for the fiscal year ended June 30, 1912. Pp. 88. Washington, 1913.—The general character of the work accomplished by the Bureau of Mines has been explained in the notice of the first Annual Report (see vol. xxxiv, p. 305), and in earlier notices in this Journal. This second Annual Report shows the activity of the department, and gives a clear impression of the progress it is

making in various lines, particularly with reference to safeguarding the lives of those engaged in mining and in insuring economy in the development and use of fuels and other mineral resources. For example, a series of investigations of explosions has been carried on so that now the type of "permissible explosives" in use has increased up to 13,000,000 lbs. in 1911. From this and other related work comes the result that there has been, in the past two years, a considerable reduction in the number of lives lost in the coal mines in the country from explosions, although the number is still far too large. Mine rescue work has also been further developed; the investigation of mines, as well as laws and regulations for safety in mines, have made progress in many States. Fuel investigations have brought much benefit to the Government, as will be seen from the fact that the fuel purchased under the advice of the Bureau in 1912 had a value of some $8,000,000. The amount of money expended by the Bureau up to June 30, 1912, was nearly $476,000, of which $312,000 was used for investigating mine accidents, $100,700 for testing fuels, $7,200 for inspecting mines in the Territories, and the remainder for general expenses, books, and publications. The total number of employees is 304.

Recent publications (see vol. xxxiv, p. 405) include the following:

BULLETINS.—No. 43. Comparative fuel values of gasoline and denatured alcohol in internal-combustion Engines; by R. M. STRONG and LAUSON STONE. Pp. 243; 34 tables.

No. 45. Sand available for filling mine workings in the Northern Anthracite Coal Basin of Pennsylvania; by N. H. DARTON. Pp. 33; 8 plates.

No. 46. An investigation of explosion-proof Motors; by H. H. CLARK. Pp. 44; 6 plates.

No. 49. City smoke ordinances and smoke abatement; by S. B. FLAGG. Pp. 55.

Also Technical Papers, Nos. 25, 27, 28, 29, 32; Miners Circulars, Nos. 9, 10, 11.

3. *Cambrian Brachiopoda;* by CHARLES D. WALCOTT. Monog. LI, U. S. Geol. Surv., 2 vols., text and plates, pp. 872, text figs. 76, pls. 104, 1912.—Dr. Walcott has had this monumental monograph on the Cambrian brachiopods of the world, his *magnum opus*, in hand since 1898. In it are described 536 species and varieties, grouped in 44 genera and 15 subgenera. Incidentally 43 Ordovician forms are also defined. These 579 species are illustrated by a great wealth of excellent photographs (retouched by Miss Wieser), of which there are upward of 4500. Of these species 361 occur in North America, 132 in Europe, and 44 in Asia. In the Lower Cambrian there are 32 genera and 116 forms, showing clearly that the class Brachiopoda had its origin far earlier in time; it will not be surprising to find such as far back as the Middle Proterozoic. The great bulk of Cambrian brachiopods are inarticulate, phosphatic-shelled forms, and we

find that the maximum of their specific differentiation occurred in the Middle Cambrian, where there are 31 genera and 335 species. In the Upper Cambrian there are 224 forms. The great bulk of differentiation took place in the four families Paterinidæ, Obolidæ (main stock), Acrotretidæ, and Billingsellidæ, though there are 14 families of brachiopods in the Cambrian.

On page 160 there is a very interesting table giving the species as they occur in the different types of sediment. Out of 500 forms only 150 have been found in more than one kind of sediment. In limestone occur 310 forms, in shale 199, and in sandstone 240. Common to limestone and sandstone there are 44, to limestone and shale 50, to shale and sandstone 28, and to all three types of sediment 33. We see therefore the justification of the author's conclusion, that as a rule "each species is confined to one type of sediment" (159). The "facies" is hence an important factor in paleontology.

Great pains has been taken to locate each fossil in the geological scale in such a way that future paleontologists can always determine the detailed horizon, even though the classification of the formations changes fundamentally. In the same way the bibliography of each species is annotated so as to give the student the essentials in each reference.

Fossil brachiopods preserving the setæ fringing the mantle are exceedingly rare, and one is figured here on page 362 as *Iphidella pannula.* It is from the Burgess shale of British Columbia, the locality that has furnished Dr. Walcott with so many other wonderfully preserved fossils.

The general shell characters of the Brachiopoda are described on pages 296–315, the evolution and classification on pages 316–326, and the genera and species on pages 327–810.

This work will always be *the book* for students of Cambrian Brachiopoda and the foundation upon which all phylogenies of the lamp-shells will be built. It is all the more remarkable that a work of so great importance should have been produced by one whose time is so much occupied in administration and in the promotion of American science. C. S.

4. *United States of North America;* by Eliot Blackwelder, University of Wisconsin, Madison. (*Handbuch der Regionalen Geologie;* herausgegeben von Prof. Dr. G. Steinmann, Bonn, und Prof. Dr. O. Wilckens, Jena. VIII Band, 2 Abteilung.) Pp. 258, figs. 81. Heidelberg 1912 (Carl Winter's Universitätsbuchhandlung).—This volume, written in English, is the first to appear of the projected series dealing with the western hemisphere. The complete series is planned to cover the whole world; this work is, therefore, of unusual interest. It contains a clear and well-proportioned summary of the geology of the United States classified under the topics of morphological summary, stratigraphy and formations, outline of geological history, orographic elements, economic geology, summary of literature, table of names of formations. Geologists of the United States will find

in this a valuable reference book with references to the more valuable original papers. No doubt it will be chiefly useful, however, to scientists of other countries, who will find in it not only a summary, but a key to the voluminous literature on the geology of the United States. They will be aided in this by the clear style in which the subject-matter is set forth. J. B.

5. *Untersuchungen über die Gezeiten der festen Erde und die hypothetische Magmaschicht;* von Dr. WILHELM SCHWEYDAR. Veröffentlichung des k. k. Preusz. geodät. Institutes. Neue Folge No. 54. Pp. 58. Leipzig, 1912 (B. G. Teubner).—This is a mathematical investigation of the theory of the horizontal pendulum and its response to tidal strains in the earth. The calculations are designed to test the presence or absence of a viscous zone between an elastic crust and elastic interior. It is concluded that even a magma bed with a viscosity as high as that of sealingwax at house-temperatures and a thickness of but 100 kilometers cannot be present. The assumption in best agreement with observations is that of the presence of a layer about 600 kilometers thick, slightly ductile (coefficient 10^{13} to 10^{14}), existing beneath an outer crust 120 kilometers thick. J. B.

6. *Variations of Glaciers in 1911.*—The annual report of the "Commission Internationale des Glaciers," published in the Zeitschrift für Gletscherkunde, Vol. VII, pp. 37–47, 1912, contains less material than usual, owing to the absence of measurements recorded in North America, Asia, the French Alps, and Russia. For the Swiss Alps, Forel and Muret give a comparison of the year 1910 with the thirteen years immediately preceding, which shows that decrease in length of glaciers continues to be normal. The glaciers of the eastern Alps likewise indicate that decrease in length and volume has not yet reached its maximum; even the three glaciers of the Wildspitze, which advanced during the period 1904–10, retreated in 1911. Apparently abnormal seasons rather than a general climatic change are responsible for the forward movement or stationary condition of a group of small glaciers in this region. Of 38 glaciers observed in the Norwegian highlands, only two show increases; the others have decreased from 2 to 34 meters. In reporting on these ice masses, Oyen calls attention to the interesting fact that portions of the same glacier move with different rates and in different directions. For the western and northern coast of Norway 12 out of 28 glaciers show increase, the maximum of 50 meters being in the Buarbræ valley; while the maximum decrease, Lodalsbræ, amounted to 19 meters. The Frostis glaciers and those on the Okstind mountains, 8 in number, indicate increase. H. E. G.

7. *New Zealand Department of Mines, Geological Survey Branch,* P. G. MORGAN, Director. *Bulletin No. 12* (*New Series*): *The Geology of the Dun Mountain Subdivision, Nelson;* by JAMES MACKINTOSH BELL, EDWARD DECOURCY CLARKE, and PATRICK MARSHALL. Pp. 71; pls. I–IX; plans, 4; maps, 4; Geological sections, 3; Wellington, 1911.—The survey of the Dun

Mountain area was concerned mainly with a study of the ultrabasic igneous rocks and associated copper deposits in the valley of Roding river. The rock types described and analyzed include Dunite, Harzburgite, Websterite, Rodingite (of which an extended discussion is given), Diabase, Diorite,—all intrusions of post-Jurassic age. Copper occurs in a belt of serpentinized basic and ultrabasic rocks, fifty-five miles long. The original mineral of the lodes is believed to have been cupriferous pyrrhotite. The table of formations shows sediments of Jura-Trias and Miocene age, but an absence of palæozoic strata previously reported from this locality. Upper Jurassic is given as the date of a period of extensive folding, repeated with less intensity in post-Miocene times. As with Bulletin 14, this report has a meagre treatment of physiography, in spite of the evidence from rock terraces and similar features that interesting problems await solution. The New Zealand Survey reports have, in general, been characterized by fairness in division of space among various branches of geological science, and it is to be hoped that no marked change in this respect is contemplated. H. E. G.

8. *Bulletin No. 14. The Geology of the New Plymouth Subdivision, Taranaki;* by Edward DeCourcy Clarke. Pp. 58; 5 maps; Wellington, 1912.—The New Plymouth area exhibits strata of Tertiary age in which are included coal beds, also lavas and tuffs dating from Miocene and Pliocene times. The Pleistocene igneous mass of Mount Egmont constitutes the most prominent topographic feature. The report is chiefly concerned with detailed descriptions of an oil locality, apparently of more scientific than commercial value. Eleven analyses of igneous rocks, minerals, oil, and a list of fossils are features of Mr. Clarke's report. The absence of a fuller discussion of the physiography is to be regretted. H. E. G.

9. *Determinative Mineralogy with Tables for the Determination of Minerals by Means of their Chemical and Physical Characters;* by J. Volney Lewis. Pp. 151; 68 figures. New York, 1913, Wiley & Sons.—It is refreshing to find among the many determinative mineral tables that have appeared recently a book like this which lays the proper emphasis upon chemical tests. This volume contains brief introductory sections upon Apparatus, Reagents, Use of Blowpipe, Reactions for the Elements, Crystallization, etc. The tables themselves in their main arrangement follow closely the well-known Brush-Penfield Tables. Fewer minerals have been treated and the description of the tests has been much condensed. The only criticism of the book might be that this condensation and the consequent abbreviation of terms had been carried a little too far. W. E. F.

10. *Dana's Confirmation of Darwin's Theory of Coral Reefs;* by W. M. Davis. *A Correction.*—On p. 179 of the above article, the first reference (*) at the bottom of the page belongs to the word *horizontal* in line 3; the second reference (†) belongs to the word *describes* in line 4 (not *describes* in line 8).

11. *Wissenschaftliche Ergebnisse der Deutschen Zentral-Afrika-Expedition, 1907–1908, unter Führung Adolf Friedrichs, Herzogs zu Mecklenburg. Band II. Botanik.* Edited by J. Mildbraed. Leipzig (Klinkhardt & Biermann).—The present publication, devoted to the botanical results of the German expedition into Central Africa, is issued in separate parts. Five of these, dated 1910–1912, have already appeared, and others are apparently to be expected. The first part, comprising 87 pages and 10 plates, treats the Pteridophyta, the Coniferæ, and the Monocotyledonæ; the second part, 88 pages and 5 plates, describes the Cryptogamæ Thalloideæ, and the Bryophyta; the third part, 94 pages and 15 plates, includes a portion of the Dicotyledonæ-Choripetalæ; the fourth part, 150 pages and 16 plates, describes a portion of the Dicotyledonæ-Sympetalæ ; while the fifth part, 87 pages and 11 plates, contains a second series of the Dicotyledonæ-Choripetalæ. In addition to the plates the second part is illustrated by 47 text-figures and the fourth part by 8 text-figures. With the exception of a short paper on poisoned arrows from Kilo, the contributions are entirely taxonomic in character and are the work of numerous specialists, most of whom are resident in Berlin. A large number of new species are described, and these, as well as many of the species already known, are accompanied by critical remarks. Even in its incomplete form the work represents a valuable addition to the numerous publications on African plants which we owe to German investigators.

A. W. E.

III. Miscellaneous Scientific Intelligence.

1. *Transactions of the Astronomical Observatory of Yale University, Vol. II, Parts III and IV. Parallax Investigations of 41 Southern Stars mainly of large proper motion ;* by Frederick L. Chase, Acting Director, and Mason F. Smith, Assistant. New Haven, 1912 (Published by the Observatory).—The work on parallax with the heliometer of the Winchester Observatory up to the resignation of Director Elkin was confined to the Northern Hemisphere, and has already been noticed in detail in this Journal.

The present volume presents the results of a campaign planned to occupy two years, and completed precisely within that limit ; consisting of measures of 41 stars between the equator and latitude 13° south. For most of these stars no measurements for parallax had ever been made when this work was undertaken. All have proper motions of 0·5″ or more except five of the second magnitude. Sixteen complete sets of observations have been taken upon each, distributed in groups of four, eight and four, except that in three cases two sets are lacking from the middle group. The results obtained seem even more consistent and free from suspicion of systematic error than the previous results of the same observers, if that be possible. There is found here the same relation between proper motion, magnitude and parallax as in the larger list of northern stars.

In part IV the catalogue previously published is revised and extended to include this later work, so that it shows the entire fruit of the parallax investigation of the Winchester Observatory on 238 stars. W. B.

2. *Bedrock, a Quarterly Review of Scientific Thought* (Constable & Co., 10 Orange st, London, W. C.).—The January number of "Bedrock" (No. 4) contains, among other important articles, one by Elie Metchnikoff on the warfare against tuberculosis; by Professor J. Joly on pleochroic halos; by Sir Bryan Donkin on science and spiritualism; by Eric Pritchard on the milk problem; and by H. H. Turner on "How could I prove that I had been to the South Pole?"

3. *Outline of Courses in Botany, Microscopy, and Pharmacognosy;* by HENRY KRAEMER, Ph.B., Ph D. Pp. 50. Philadelphia (J. B. Lippincott Co.).—Outlines of laboratory work for students in schools of pharmacy, based on the author's "Text-Book in Botany and Pharmacognosy" (already noticed in this Journal) and illustrating the courses given in the Philadelphia College of Pharmacy. Instruction is expected to extend through three years, and covers botany the first year, pharmacognosy of drugs of the U. S. Pharmacopœia the second, and pharmacognosy of important non-official drugs the third. A. L. D.

OBITUARY.

Dr. F. TELLER, chief geologist of the K. K. Geologische Reichsanstalt in Vienna, died on January 10 in his sixty-first year.

M. L. P. CAILLETET, the French physicist, died on January 5 in his eighty-first year. His work on the liquefaction of the so-called fixed gases in 1877 and 1878, with that of Pictet, formed one of the most important epochs in the history of Physics.

M. L. TEISSERENC DE BORT, the able French meteorologist, died on January 6 at the age of fifty-four years.

Dr. PAUL GORDAN, the eminent German mathematician, died on December 21 at the age of seventy-four years.

Professor ROBERT COLLETT, the Norwegian zoologist, died in January last at the age of seventy years.

Dr. AUGUSTUS WITKOWSKI, Professor of Experimental Physics in the University of Cracow, died on January 21 at the age of fifty-eight years.

The EARL OF CRAWFORD (James Ludovic Crawford), the astronomer, president of the Royal Astronomical Society in 1878–79, died on January 31 at the age of sixty-five years.

WILLIAM GREENWOOD WRIGHT, the entomologist, died on December 1, 1912, in the eighty-third year of his age.

Dr. OTTO SCHOETENSACK, the German anthropologist, died on December 23 in his sixty-third year.

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VOL. XXXV. APRIL, 1913.

Established by **BENJAMIN SILLIMAN** in 1818.

THE

AMERICAN
JOURNAL OF SCIENCE.

EDITOR: EDWARD S. DANA.

FOURTH SERIES

VOL. XXXV—[WHOLE NUMBER, CLXXXV].

No. 208—APRIL, 1913.

NEW HAVEN, CONNECTICUT.

1913.

THE TUTTLE, MOREHOUSE & TAYLOR CO., PRINTERS, 123 TEMPLE STREET.

Published monthly. Six dollars per year, in advance. $6.40 to countries in the Postal Union; $6.25 to Canada. Remittances should be made either by money orders, registered letters, or bank checks (preferably on New York banks).

THE

AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

Art. XXX—*The Circulatory System in the Halemaumau Lava Lake during the Summer of 1911;* by Frank A. Perret.

The degree of activity at Halemaumau varies between comparatively narrow limits within which, nevertheless, we may, for convenience, distinguish three principal phases, viz.: the sub-normal, normal and super-normal.

In the first case, the lava—generally very low in the pit—may be entirely covered by a solid, non-luminous crust, or it may be altogether absent as the result of a so-called "breakdown," by which inelegant epithet is meant a subterranean lateral outflow of lava from the conduit, thus draining the overstanding crater of its liquid contents.*

At the other extreme, under super-normal conditions there is a lake of liquid lava filling the crater basin from side to side, whose temperature and mobility are of the highest order. Fountains play over the entire surface and the ascending gases so thoroughly stir and heat the mass of liquid that the surface remains quite free from crust.

Between these extremes—abnormal as regards their distribution in time—we find a condition which frequently prevails for months, and even years, with occasional variations and which may, therefore, for our day, be considered as the normal state of activity. The supply of heat is such that the temperature of the lava oscillates about the point of its congelation in contact with air or rock, with a tendency to fall below it. The condition might be described as a semi-liquid phase. There is a lake of liquid lava the dimensions of which are restricted by

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*It will be seen that this latter condition does not indicate any general lessening of the volcano's activity but only as regards the terminal crater.

a surrounding "shore" of solid material congealed to the sides of the pit. The lake is active by the continuous emission of gas and especially through the irruption, and eruption, of very large bubbles which, coalescent in the depths of the conduit, rise with great buoyancy and form those beauteous fountains of lava, to the study of which a preceding paper has been devoted.* This particular form of activity is, however, of an intermittent character and is limited to certain portions of the lake upon whose general surface there forms, by cooling in contact with air, a film or skin, flexible while thin but often thickening to a solid crust which is brittle and readily broken by uneven pressure. As these congelations occur in spite of the ordinary supply of juvenile gas, it is highly probable that, were it not for some other preventive cause, the inward consolidation from the walls and the downward incrustation from the surface would continue progressively until the entire mass became solid.

This preventive cause consists of a grand movement of translation in the lava of the lake—a powerful system of circulation which stirs the entire mass of liquid, impeding deposition upon the walls and preventing the formation, for any length of time, of a thick, immovable crust upon the surface. In importance, therefore, this phenomenon will be seen to be second to none and to merit the devotion of a paper to its exclusive study.

It is natural, in such cases, to seek analogy in some familiar or easily tried experiment, and this is here found in a vessel of water heated from below. Expanded by the heat, the lower liquid rises to the surface, spreads and descends by the cooler sides, and when ebullition occurs, the expansive effect of the gas bubbles, together with their buoyancy, adds ascensional power to the rising column, thus establishing a system of convection by which the entire mass is stirred—why not, therefore, under essentially similar conditions in the crater, a similarly simple and easily explainable principle of action? But it is in precisely this manner that many long-lived errors have crept into science, whose history has shown the necessity of investigating the phenomenon itself instead of studying an imitation, however temptingly analogous.

The merest glance at the normal lava lake at Halemaumau suffices to show that it has a longer and a shorter diameter and that the surface material is moving in the general direction of its length. We shall see later that these conditions are not fortuitous but are the necessary consequence of the working principle of the circulatory system. During the entire summer of 1911, excepting for a few hours on August 9th and

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* This Journal, February, 1913.

August 11th, the flow of surface lava was from under the bank at the western end of the lake, where it was evidently rising from below, to a number of points at or near the eastern end, including the localities of the large fountains, where it was intermittently or continuously descending.* Now, we know that the basin does not concentrically overlie the conduit, but is greatly extended to one side (the west) as though excavated in that direction. We might deduce this conformation by the localization of the large lava fountains in the eastern half of the lake, these being due to the rapid ascent of great gas bubbles directly from the conduit, but the survey of the empty crater basin by Baldwin in 1902 also showed the eccentric position of the conduit, it standing then, as now, under the eastern half of the crater cavity. But, as the reader will already have perceived, there is here an apparently anomalous state of things, viz.: that it is in the eastern half of the lake, which overlies the conduit and where the large bubbles rise and form the fountains, that the lava is *going down*, while, per contra, it is rising—quietly and free from large gas bubbles—at the western end of the lake, as far as possible from the conduit itself. We should, therefore, have already been far astray had we based our study on the behavior of convection currents in a simple liquid.

Let us now attentively observe the surface material in its passage across the lake. Issuing in clear incandescence from under the western bank the surface is instantly chilled on coming into contact with the outer air and a film is formed which, from its appearance, has been generally designated as "scum." The word is inappropriate as regards the nature of the material which is that of a continuous skin, flexible at high temperature and very tough. Being formed quickly it is non-crystalline and of a high degree of diathermacy which, however, is limited by entangled gas vesicles. Congelation to the under surface will, therefore, continue but with decreasing rapidity until crystalline deposition begins, whereupon the radiation of heat from below will be greatly retarded and the process of thickening will proceed more slowly but with the formation of a true crust of lava rock. As the surface layer spreads out from the place of issue into the body of the lake the skin is pulled apart in irregular lines through which glows the bright lava below as shown in the night view (fig. 1). It is important to note that, although the lava rises quietly here at the west end of the lake and is free from the great gas bubbles which form the large fountains, it is, nevertheless, highly charged with minute gas vesicles some of which, coalescing, burst

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* The records show that, for a number of years, this condition has quite generally prevailed.

through the less resisting "bright lines," forming tiny fountains, and the rest, accumulating under the crust, issue as a continuous gas flow through innumerable holes and rents, burning in the air with the steady, pointed, blow-pipe flames described in the paper on lava fountains.

On arriving at the eastern portion of the lake the lava has, therefore, suffered three principal modifications, all of which contribute to one grand result which, as we shall see, is the key to the problem of the circulation—it has lost its gases, it has lost heat and has become, in part, solidified. The net result of all this is that the surface layers are denser and heavier than the rest of the lake material and therefore *tend to sink.* This is most evident in the crust itself which is a solid crystalline rock, pieces of which sink readily in the liquid as is forcibly shown during the frequent upward oscillations of the lake. It might reasonably have been supposed that a rising lava column would raise its floating crust but this it does not do. The crust breaks by uneven pressure from below and the lava rises through the cracks, up-tilting the broken pieces which readily sink edgewise in the liquid. The rising lava does not raise the crust but breaks it up, rises through it, and sinks it.

Fig. 1.

Fig. 1. Night view. Bright lines formed by the pulling apart of the crust. Western half of lake. From the North.

Now, it is obvious that the crust, ordinarily, cannot sink as a horizontal sheet, but whenever it is enabled to turn and sink vertically it will do so, and this vertically descending material should be understood to include with the crust itself, whether flexible and bending or brittle and broken, the immediately underlying sheets of gas free, partially cooled and more or less viscous lava which may all be comprised in the general term "heavy surface layers."

Let us now suppose these surface materials moving normally eastward, when a lava fountain bursts into play. A great dome of glowing liquid is thrown up, boiling furiously, while a cloud of bluish vapors, rising above it, indicates the escape of gases, the flash of whose flame is invisible by day. The fountain lava, cooled and condensed, then subsides into the lake—whose surface level is already depressed locally by the absence of displacement of the great gas bubbles just vanished—and, by its momentum and greater density, continues to sink while the surface layers, surging inward from all sides, turn downwards and follow, often for a considerable time.

FIG. 2.

FIG. 2. Showing striation of lake surface by division of flow. General flow is from farther end towards the observer. View looking West.

But the general trend of the surface current is toward the several caves or "spatter-grottoes" situated at the margin of the lake, the division of flow producing a striation of the surface skin, occasionally, but not frequently, as complicated as that shown in fig. 2. These grottoes are, in part, eroded in the banks by the large bubbles of juvenile gas ascending from the conduit, but are chiefly formed by the arching over of a roof built of the congealed spatterings of lava scattered by the bursting bubbles of gas. They are, therefore, peripheral fountains, as contrasted with the central type, and their action, while more nearly continuous, is essentially similar, producing a lower level within the grotto into which the surface layers flow, turn downward, and descend. Once this action is started it will be accelerated and maintained by the downpull of the vertically descending heavy layers which act as a sort of semisolid syphon of which the long arm is the descending sheet and the short arm is represented by the surface layers, actually longer but easily drawn by reason of their horizontal position. The suction is sometimes so strong as to produce a veritable maelstrom with a local surface flow resembling a mill-race, and it is this powerful downflow of the heavy surface layers which is the immediate cause of the great movement of translation and of the whole system of circulation. No mere difference of surface levels could produce such rapid flows—often reaching four meters per second in a mill-race and frequently exceeding sixty meters per minute on the general surface of the lake—while convection, in the sense of a rising column of heated and vesiculated lava, although not absent as we shall see later, plays a rôle which must be considered as secondary.

The indirect but true *primal* cause lies, of course, in the ascent of the great bubbles and it will seem strange to the reader, as it has to observers, that these rise where the lava is descending. In reality, however, it is the lava which flows to and descends at those localities where the level is lowered by the escape of the gas bubbles. William Lowthian Green, in attempting to account for most of the Hawaiian phenomena on a non-gaseous basis,* held that the violent jetting of the lava at the places of descent was due to air being carried down with the lava and, expanded by the heat, again bursting its way to the surface. This ingenious explanation is negatived by the fact that the escaping gas burns in contact with the atmosphere, the flames, under certain circumstances, being always and easily visible at night. Jets of flame five meters in length often flash from a spatter grotto upon the bursting of a large gas bubble within while smaller jets burn steadily at broken portions of its overhanging roof. The present writer

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* "Vestiges of the Molten Globe," by Wm. Lowthian Green, Honolulu, 1887.

has also observed that when, by a combination of circumstances, a downflow of lava is produced at a location where there are generally no large gas bubbles to cause jetting or spattering, the downflow proceeds with perfect quietness. This was notably the case for a short time on the eleventh of August, 1911, when, by some means, a downflow was started along a line stretching entirely across the lake not far from its western end. The crust was sufficiently flexible to be bent downward without breaking and the pull of the vertically descending heavy sheets was sufficient to draw the surface layers inward from either side and down into this semi-liquid fissure, the syphon-like action continuing for several hours without any jetting whatever. It is clear that the vertically descending crust must be melted at no great depth, but the fused material also will be denser than the average gas-vesiculated lake substance and the action is the same. This is also seen at some spatter grottoes where the radiant heat is sufficient to partially melt the crust on the in- and down-flowing surface lava even before it has quite entered the grotto, yet the heavy material sinks and maintains the flow, although the crust, as such, no longer exists.

As regards the ascent of gas in those localities where the lava is going down, it is not necessary to believe that the bubbles always struggle upward through the descending lava—they may rise to one side of the downflow or between it and the wall of the basin. Large gas bubbles, by their extreme buoyancy, rise very rapidly through the very mobile lake material without carrying the lava with them to any extent and they may even rise through a slowly descending current of the liquid. In this case the opposing forces are often in equilibrium, the surface lava surging toward the grotto, then stopping and then again advancing, like the movement of a cinematograph film. It is the very *small* gas bubbles which, themselves incapable of rapid ascent, may, by their vesiculation of the lava, cause it to rise "en masse" and this mode of action plays its part in the scheme of circulation.

Before taking a comprehensive view of this we must consider a detail which, during the early summer of 1911, formed the most extreme manifestation of relative movement in the lava of the lake and which constituted, while it lasted, the principal element of the circulation. A large cavity had been eroded in the mass of a floating island of rock, extending from the bottom vertically upward to a point under the saddle between the two principal portions of the island. This cavity was open at the lake surface on the north (fig. 3), and also on the east side, in the form of a grotto within which the lava could be seen, free from crust, and in communication with the outside material. Suddenly a fountain would play within the grotto and, subsiding, produce a lower level in the interior, whereupon the outside lava would flow into the grotto. The peculiar conformation prevented the entrance of anything but *surface material*, which is denser than the rest of the lake substance, thus producing a still lower interior level and causing a downpouring of the heavy crust and surface lava whose momentum as a freely falling mass was increasingly effective in beating down the inner level. The result was a cavity, empty as far down as could be seen from the place of observation on the north brink of the crater, and into which a magnificent cascade of lava was freely pouring from either side, the inner walls glowing in full incandescence, the two cascades clashing amid fiery spray, and the whole forming a spectacle the beauty of which can with difficulty be imagined, even by those who are familiar with the sight of active lava. The difference of internal and external level could not have been less than five meters and it may well be that so great a dislevelling would not be possible without the aid—as suggested by my colleague, Dr. Shepherd—of some aspiration at the lower end of the cavity and which might have resulted from a powerful downflow between the island and the shore, the exist-

Fig. 3.

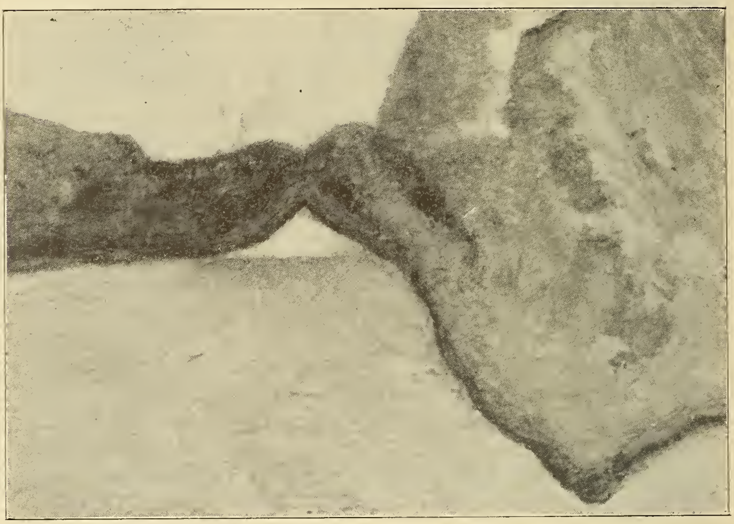

Fig. 3. Grotto and cavity under Floating Island into which surface-lava was flowing in a continuous cascade.

ence of which was indicated by a mill-race at the surface. However this may be, the cause of the one is the cause of the other, but the island grotto with its cascades falling free must certainly represent the maximum grade of inter-circulation of the lake lava. The cascades would continue to flow for several hours when the action would cease with the rise of the inner level to equilibrium with the rest of the lake, remaining thus until again disturbed by gas action from within.

Fig. 4.

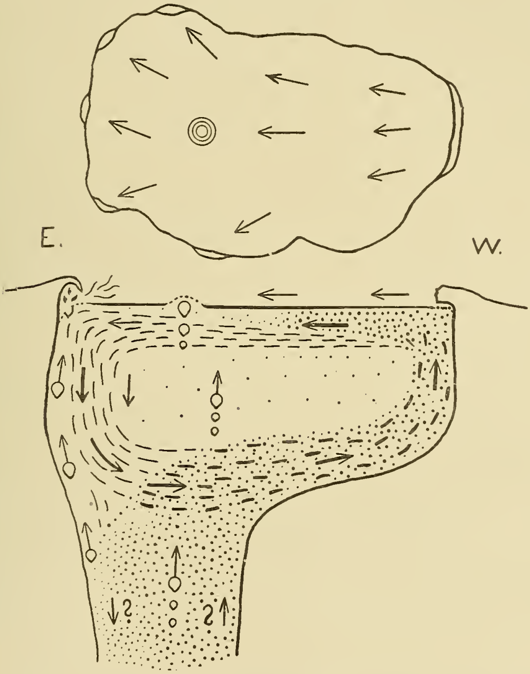

Fig. 4. Diagrammatic plan and East-West section of Lava Lake, showing scheme of circulation.

We are now in a position to take a general view of the entire system of circulation as shown diagrammatically in fig. 4. The island and its cascade grotto are here omitted as having constituted an altogether exceptional phenomenon and to avoid complication, the downflowing phase and its mechanism being represented by a spatter grotto in the east bank of the lake.

The lava is shown issuing from under the western* bank

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* The west is here placed at the right, as the usual point of view at Halemaumau is from the north. See fig. 1.

highly charged with minute gas vesicles which gradually rise and escape during the passage across the lake, the flow being then represented in the diagram by short lines. The crust grows in thickness and, on arrival at the eastern end, the surface layers—cooled, condensed and gas-free—enter the spatter-grotto and sink vertically as a continuous heavy sheet to form and maintain the powerful syphon effect which is the mainspring of the circulatory system.

Arrived at the bottom and turning westward the current passes over the mouth of the conduit from which are rising the vesicles of juvenile gas. The large, intermittent, fountain-forming bubbles rise rapidly and buoyantly to the surface, suffering but little deviation by the horizontally moving strata —of which the one corrects the other—but the innumerable minute vesicles can rise but slowly and these are entrapped by the west-flowing lava, which is thereby re-heated and re-vivified. In this condition it has acquired ascensional power and—as it must, in any case, rise to balance the descent at the east—this power is thus added to the other forces in maintaining the circulation. But it is important to note how comparatively *feeble* is this ascensional power of the gas-vesiculated lava which, instead of rising directly, is deflected to the extreme end of the lake by the powerful effect of the eastern downflow.

The critical reader may here move the objection that, for a paper wherein it is sought to confirm each statement by actual observation, confident mention is now being made of a westward return current in the lower part of the lake whose existence, however strongly indicated, is, nevertheless, deduced. And we are, therefore, fortunate in being able to record a circumstance which shows the reality of this undercurrent almost as conclusively as direct vision would have done. At the time of the sinking of the island of 1911, as described in the preceding paper of this series, a quantity of gas was evolved which formed and inflated a floating cylinder of black lava, below which the sunken mass of the island hung downward in the lower part of the lake, remaining attached by one end to its floating buoy. The sinking occurred at the east end of the lake and the cylinder at once began to make its way westward *against the surface current*, it being towed by the mass of the island suspended in the west-flowing undercurrent. Nor is this all, for, on approaching the west bank, the sunken mass was again brought to the surface, a point of the original island being seen and photographed emergent from the lake. This re-flotation was, no doubt, caused by the rising, gas-charged lava current of the west end and, no sooner was it accomplished, when the whole system proceeded eastward again, being now entirely under the influence of the surface current.

The reason why the normal lava lake will have a greater length in some direction away from the conduit, and why the lava will circulate in the direction of its length, is now made beautifully clear by the present hypothesis. From the diagram it will be seen that the downflow at the east consists of the coolest lava which, even if it does not consolidate to the walls by reason of its rapid motion, is, at all event, quite lacking in re-fusing power, while the large hot gas bubbles only rise at intervals—the wall at this end remains, therefore, much after

FIG. 5: A (above) and B (below).

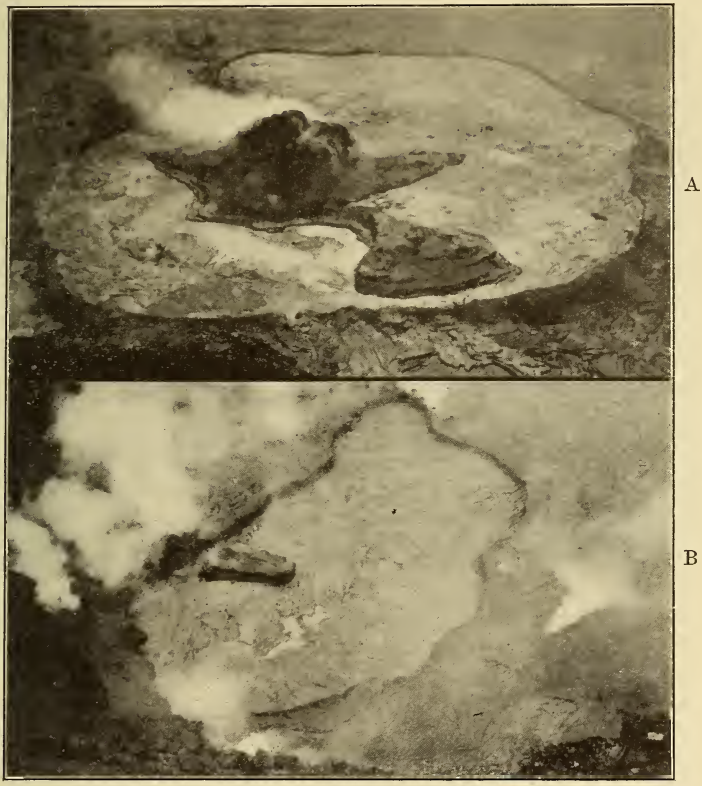

FIG. 5. Comparative views. A. July 5, 1911. B. Sept. 9, 1911; 25 meters lower. Showing change of form through lesser activity.

the manner of a simple pit-crater. On the other hand, the lava in its passage over the conduit has become re-heated and re-vivified and will not only resist congelation to the walls but may often be capable of re-melting them and thus to actually excavate an extension in the direction of its flow. We may confidently say that a continuance of normal conditions will inevitably produce an oblong lake with circulation in the direction of its length and, in view of the fact that, under waning conditions of activity, consolidation will occur at the sides while it will be impeded at the ends, we may go further and state that, as conditions approach the sub-normal—especially after a normal phase—the lake will be longer and narrower, while an approach to super-normal activity will result in a more nearly circular form. See fig. 5.

Fig. 6.

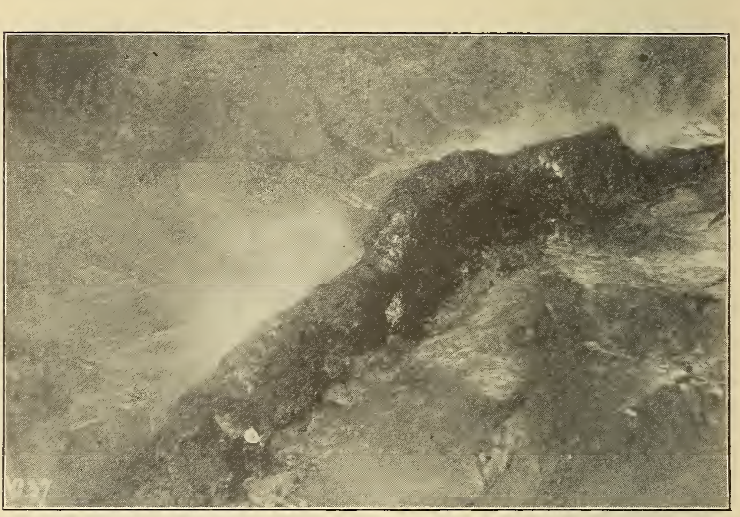

Fig. 6. Telephoto view of a typical spatter-grotto.

A final question, of great importance but difficult of solution, is whether or not the conduit proper is interested in the scheme of the lake's circulation,—whether, that is to say, a portion of the downflowing lake lava descends into the conduit with a corresponding rise at the other side from the conduit to the lake, as indicated in the diagram by the arrows marked with interrogation points? Daly, in a beautifully written paper*—with some of whose conclusions regarding Kileauean phenomena the present writer does not, however, quite agree—is of the opinion that convection, in the sense of the proper motion of a mass of highly vesiculated lava, may "stir the magma column to great depth and with considerable rapidity." The idea of the extension of the circulation to the conduit would be very convenient as making easy the question of heat maintenance and especially as tending to explain the well-known *migration of conduit and crater* by the downflow of cooled and passive material at one side and the rising of hot and active lava at the other. Where all is conjecture, however, it may be but fair to state that there seems to be some reason for believing the actual exchange of lava between conduit and crater to be quite limited—sufficiently so to permit the material in the crater basin to acquire, by being ceaselessly worked over in contact with air and water and made the recipient of the mass of gas vesicles rising from the conduit, a different consistency to that of the lava in the conduit.

However this may be, it seems certain that the fundamental cause of heat maintenance in the entire lava column, as well as of all the dynamic phenomena, lies in the supply of juvenile gas, and that the immediate cause of the circulation in the crater lake is the formation of heavy surface layers which tend to sink.

Posillipo, Naples, Feb. 7, 1913.

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* "The Nature of Volcanic Action," Reginald A. Daly, American Academy of Arts and Sciences, vol. xlvii, No. 3.

Art. XXXI.—*The Oligocene of the Roanne Basin and Its Vertebrate Fauna*;* by Charles Depéret.

As shown by the studies of Le Verrier, the Tertiary basin of the Roannais (a former province near Lyons, France) comprises a basal series of sands, gravels and clays, supposed to be of Stampian age, and an upper series of calcareous marls corresponding to the Aquitanian, the whole being practically barren of fossils.

During recent years important paleontological discoveries have been made in consequence of the extension of the earthenware industry in the vicinity of Mayolet, Briennon, Mably, and especially La Bénissons-Dieu. For the purpose of arriving at a more precise correlation of these deposits a reinvestigation has been made by the present writer of the Oligocene strata as they occur in the Roanne basin, where they form a monocline dipping toward the northwest, and present the following section (arranged in ascending order):

4. Calcareous marls of Saint-Germain-Lespinasse, extending between that place and Digoin, and yielding at the latter locality remains of an *Anthracotherium* characterized by having digits of sub-equal length, and apparently belonging to the same species as that which occurs at La Bénissons-Dieu.

3. Strata of Mably and La Bénissons-Dieu, consisting of a bottom bed of sands, which graduates upward into clays. From the latter of these two localities have been obtained excellently preserved remains (including the entire cranium, jaws, limbs, etc.) of a large *Anthracotherium*, the lateral digits of which are much less reduced than in *A. magnum* (= *A.* cf. *bumbachense* Stehlin). There have also been found here two species of *Aceratherium*, one of which is very large (*A. filholi* Osborn), the other very small (*A. albigense* Roman); and besides these there occur remains of a species of *Cainotherium*, one of *Dremotherium*, as well as Crocodiles and Chelonians.

2. Reddish clays of Briennon. These have yielded at Briennon remains of *Entelodon magnum* Aymard, and at Mayolet an inferior molar of the small *Anthracotherium alsaticum* Cuvier.

1. Nonfossiliferous bands of gravels, sands and conglomerates.

The strata constituting the above section may be correlated as follows: Divisions 1 and 2 are referable to the Sannoisian (Lower Oligocene), the few known fossil forms being identical with those occurring in the Lower Oligocene asphalt deposits of Lobsann, in Alsace. Division 3, or the strata of Mably and La Bénissons-Dieu, corresponds to the lower portion of the

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* A preliminary notice, to be followed by a more detailed article in the Bulletin de la Société Géologique de France. Translated by C. R. Eastman, Carnegie Museum, Pittsburgh, Penn.

Stampian (Upper Oligocene), being well characterized by the above-named species of *Aceratherium.* The fourth member of the series, or marly limestone of Digoin, carries the same species of *Anthracotherium* as Division 3, and cannot be younger than of Middle Stampian age. There are no strata, therefore, in the Roanne basin that can be properly referred to the Aquitanian (or Lower Miocene), as has formerly been thought.

Postscriptum added by the Translator.

As a result of Professor Depéret's determination of the vertical succession of Tertiary strata in the Roannais, Lyonnais, and adjacent regions, it is now possible to synchronize more precisely than was formerly the case the different mammiferous horizons throughout various parts of France and elsewhere. One may compare, for instance, the tabulation given above with the following arrangement of mid-Tertiary beds in the Paris Basin, which is adopted by Paul Lemoine in his recent work, La Géologie du Bassin de Paris (1911):

MIOCENE.	
Tortonian	Faluns de l’Anjou. Faluns de Touraine.
Helvetian	Sables de Sologne.
Burdigalian	Sables de l’Orléannais.
Aquitanian	Calcaires de l’Orléannais.
OLIGOCENE.	
Chattian	Meulières de Montmorency.
Stampian	Sables de Fontainebleau.
Sannoisian	Calcaire de Brie.

The general correspondence of these time divisions and depositions with North American formations will appear from the table appended below, which has been drawn up by Mr. O. A. Peterson, of the Carnegie Museum, from the most recent data available, including the results of his own field studies and those of the late Mr. Hatcher:

In South Dakota, as is well known, the Oligocene is much more extensively developed than in the Nebraska region, and comprises three clearly marked faunal zones, which have been named as follows: (1) Titanotherium beds (= Lower White River or Chadron beds); (2) Oreodon and Metamynodon beds (= Middle White River); and (3) Leptauchenia and Protoceras beds (= Upper White River). The middle and upper members of the White River are grouped together by some geologists under the term of Brule formation, which attains a maximum thickness of about 400 feet, or about double that of the lower member (= Chadron or Titanotherium beds). In

Table of Mid-Tertiary Correlatives.

European Stages	Nebraska Section	John Day Basin
Upper and Middle Miocene	Upper Harrison beds	Mascall formation and Columbia Lava [Interval of erosion]
Lower Miocene (Aquitanian)	Lower Harrison beds Monroe Creek beds Gering sandstone	Upper John Day beds Middle John Day beds
Upper Oligocene (Stampian) Lower Oligocene (Sannoisian)	Leptauchenia beds and underlying Oligocene strata (Chadron beds and Brule formation), of much less thickness than the equivalent White River beds of the South Dakota section.	Lower John Day beds, transitional between Oligocene and Miocene, of continuous deposition with the Middle John Day beds, and resting unconformably upon the Clarno beds of undoubted Eocene age.

South Dakota, also, the Lower Miocene falls naturally into a two-fold instead of a tripartite division as in Nebraska, the two members of the series being known as the Lower and Upper Rosebud beds. The Lower John Day beds of Oregon are of transitional character, and may be classed as either uppermost Oligocene or lowermost Miocene, the difficulty being that they are not separated from the Middle John Day beds by any apparent stratigraphic break.

An earlier and somewhat different correlation of the section in the John Day Basin than that which is here proposed by Mr. Peterson will be found in an article by Drs. J. C. Merriam and W. J. Sinclair on the Tertiary Faunas of the John Day Region (Bull. Dept. Geol. Univ. Cal., 1907, vol. v, No. 11). For the benefit of those interested in the correlation of European formations reference may be made to the following recent papers :

Dollfus, G. F.; Essai sur l'Étage Aquitanien. Bull. Serv. Carte Géol. France, 1910, vol. xix, no. 124. [The Aquitanian is here considered as Lower Miocene.]

Stehlin, H. G.; Remarques sur les faunules de mammifères des couches éocènes et oligocènes du Bassin du Paris. Bull. Soc. Géol. France, 1912, (4) vol. ix. See also his Revision of European Anthracotheres, 1910.

Glangeaud, P.; Les faciès de l'Oligocène aux environs de Bergerac et dans le Dordogne, 1912, loc. cit.

Haug, E.; La Période Néogène, in his 'Traité de Géologie,' 1911, vol. ii, fasc. 3.

Perisho, E. C., and *Visher, S. S.;* South Dakota Geol. Surv., 1912, Bull. No. 5.

Art. XXXII.—*On the Rate of the Reduction of Mercuric Chloride by Phosphorous Acid;* by G. A. Linhart.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxliii.]

In 1902 Montemartini and Edigi,* in studying the velocity of the reaction between phosphorous acid and mercuric chloride, represented it by the following equation:

$$2HgCl_2 + H_3PO_3 + H_2O = 2HgCl + H_3PO_4 + 2HCl,$$

and considered it, therefore, to be a reaction of the third order, since the concentration of the water may be considered practically constant under the conditions of the experiment. However, these investigators were unable to obtain concordant figures for the velocity constants when substituting their experimental results in the formula,

$$K = \frac{1}{2t}\left(\frac{1}{(c-x)^2} - \frac{1}{c^2}\right)$$

They then substituted their experimental results in a formula representing a reaction of the second order, but again failed to obtain constant figures. This abnormal behavior of the reaction between mercuric chloride and phosphorous acid they attributed to the effect of some initial disturbance.

Garner,† Foglesong and Wilson consider the reaction to be of the fourth order, although they represent it by the same equation as given above. They draw this conclusion not from any theoretical consideration, but because "values for the second and third order equations decrease rapidly, and those of the fourth order are reasonably constant." In the calculation of the velocity constants these investigators employ the formula,

$$K = \frac{1}{3t}\left(\frac{1}{(a-x)^3} - \frac{1}{a^3}\right),$$

which applies only to the special case where the concentrations of the reacting substances are all equal, but they use it even in cases when the concentrations of the reacting substances in their experiments are unequal. In a later number of the same Journal‡, however, Garner acknowledges the error in this procedure and states that his results will be recalculated and published in a subsequent paper. However, the recalculated results have not yet appeared in print.

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* Gazz. Chim. Ital., xxxii, 2, p. 182.

† Amer. Chem. J., xvi, 361.

‡ Ibid., p. 648.

Although the equation,

$$2\text{HgCl}_2 + \text{H}_3\text{PO}_3 + \text{H}_2\text{O} = 2\text{HgCl} + \text{H}_3\text{PO}_4 + 2\text{HCl}, \quad (1)$$

is in complete accord with the facts as far as the final result of the reaction is concerned, it fails to account for its velocity; for no one who has studied the velocity of the reaction has been able to show that it is actually of the third order as this equation would require. It is evident that if the reaction is of the third order an increase in the concentration of phosphorous acid to an amount about twenty times the theoretical quantity required to reduce all of the HgCl_2 ought to produce fairly concordant constants when the experimental results are substituted in a formula representing a reaction of the second order, since the variation in the concentration of the phosphorous acid is then very slight. Making use of this principle, the following results were obtained:

TABLE I.

HgCl_2 = 0·005 mols per liter = A T = 25°
H_3PO_3 = 0·050 " " " = B

	$x = \text{HgCl}$			
t in hrs.	in grams	in mols	K_2	K_1
4·6	0·0052	0·001104	12·3	0·0541
7·9	0·0083	0·001760	13·7	0·0541
17·5	0·0140	0·002950	16·4	0·0511
24·0	0·0167	0·003546	20·3	0·0513
42·3	0·0212	0·004500	42·5	0·0543
∞	0·0235	0·005000		

T = 60°

	$x = \text{HgCl}$			
t in min.	in grams	in mols	K_2	K_1
15·	0·0103	0·002187	10·4	0·0384
30·	0·0156	0·003312	13·0	0·0361
45·	0·0194	0·004114	20·5	0·0384
75·	0·0223	0·004734	47·5	0·0389
∞	0·0235	0·005000		

K_2 was calculated from the equation $K_2 = \dfrac{x}{\text{A}(\text{A}-x)t}$ and K_1 from the equation $K_1 = \dfrac{2{\cdot}3}{t}\log\dfrac{\text{A}}{\text{A}-x}$. It is evident from the above results that the reaction is of the first order with respect to the HgCl_2. The "initial disturbance," therefore, observed by Montemartini and Edigi in the reduction of mercuric chloride by phosphorous acid cannot be due to abnormal behavior of the mercuric chloride when sufficiently diluted (0·005 mols per liter). Since equation (1) is a correct representation of the final result, the fact that the reaction is of the first order with respect to mercuric chloride indicates that it must take place in stages. No intermediate stage is known in the change of $HgCl_2$ to $HgCl$, but between phosphorous and phosphoric acid we have the known compound hypophosphoric acid H_2PO_3.

It will be shown in this article that the first stage of the reaction is probably the oxidation of phosphorous to hypophosphoric acid.

(a) $HgCl_2 + H_3PO_3 = HgCl + H_2PO_3 + HCl$, the hypophosphoric acid then reacting with the water, especially in the presence of hydrochloric acid,* as follows:

$$\text{(b)} \qquad 2H_2PO_3 + H_2O = H_3PO_3 + H_3PO_4.$$

If we assume that reaction (b) is fairly rapid as compared with reaction (a), the concentration of the phosphorous acid at any time t may be represented approximately by $b-\frac{1}{2}x$, since for every two molecules of phosphorous acid decomposed one molecule of phosphorous acid is regenerated. The rate of the reaction between mercuric chloride and phosphorous acid may therefore be represented by the differential equation:

$\frac{dx}{dt} = k(a-x)\,(b-\frac{1}{2}x)$, (2) where a and b denote the initial concentrations of the mercuric chloride and phosphorous acid respectively, and x the amount of the reacting substances decomposed or of the mercurous chloride† or of the hydrochloric acid formed, all expressed in gram mols per liter. Setting $a = A$; $2b = B$

$$\frac{dx}{dt} = K(A-x)\,(B-x) \qquad (3)$$

K in the table below is obtained by substituting the experimental results in the integrated form of the above equation,

$$K = \frac{2{\cdot}3}{(A-B)t}\log\frac{(A-x)B}{(B-x)A}. \qquad (4)$$

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* For the decomposition of hypophosphoric acid see A. Joly, Compt. rend., cii, 110, 1886, and Jahresber. chem., i, 347, 1886. Also Amat, Compt. rend., cxi, 676.

† The fact that the mercurous chloride in equation (a) is necessarily represented by HgCl is not incompatible with the theory that the double molecule Hg_2Cl_2 is the normal one, since the HgCl may polymerize as soon as it is formed. A similar explanation may be offered for representing hypophosphoric acid by H_2PO_3 instead of $H_4P_2O_6$.

TABLE II.

$HgCl_2$ = 0·132 gram mols per liter = a T = 60°
H_3PO_3 = 0·0575 " " " " = b

t in min.	$x = HgCl$ in grams	$x = HgCl$ in mols	K
35	0·1183	0·02512	0·1200
87	0·1902	0·04038	0·0911
138	0·2471	0·05246	0·0875
183	0·2891	0·06138	0·0884
360	0·4162	0·08837	0·1163
∞	0·5417	0·11500	

It will be clear from what follows that the initial falling off and subsequent increase in the velocity coefficient K is due to the effect of hydrochloric acid formed in the reaction.

In order to determine this effect of hydrochloric acid a series of experiments were carried out in which various amounts of hydrochloric acid were present at the start. When the results of these experiments were plotted, perfectly smooth curves were obtained. See figs. I and II. Moreover, their relative position shows clearly that the reaction is accelerated by hydrogen ions.

It is, therefore, necessary to take the concentration of free acid into account. Since the disappearance of phosphorous acid results in the formation of an equivalent amount of phosphoric acid the effect of the hydrogen ions from these two acids upon the velocity of the reaction is nearly constant, and no serious error will be introduced by assuming the concentration of the hydrogen ions to be proportional to the concentration of hydrochloric acid, which may be represented by $C + x$, where C denotes the initial concentration of the HCl used.* Introducing this value into equation (2)

$$\frac{dx}{dt} = k\,(a - x)\,(b - \tfrac{1}{2}x)\,(C + x). \qquad (5)$$

Setting $a = A$, $2b = B$, $\frac{k}{2} = K$, this becomes,

$$\frac{dx}{dt} = K\,(A - x)\,(B - x)\,(C + x), \qquad \text{whence}$$

$$K = \frac{2{\cdot}3}{(A - B)\,(A + C)\,(B + C)t} \log \left(\frac{A - x}{A}\right)^{B+C} \left(\frac{B}{B - x}\right)^{A+C} \left(\frac{C + x}{C}\right)^{A-B} \qquad (6)$$

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* Although some of the hydrochloric acid combines with the mercuric chloride to form complexes, the catalytic effect of the hydrogen ions is not impaired, as these complexes, according to Leblanc and Noyes, are dissociated to the same extent as hydrochloric acid of equal molecular concentration.—Zeitschr. phys. Chem., vi, 329.

As a matter of fact the constants calculated from this equation gradually increase.* This, however, may very reasonably be ascribed to the influence of complex molecules of the types $H_2Hg_2Cl_6$, etc., which are known to form in the presence of hydrochloric acid† and which probably do not react, as such, with the phosphorous acid. Since these complexes break up with increasing dilution, the velocity coefficient as calculated by equation (6) ought to rise, as is actually the case.

It is a remarkable fact that if in equation (5) $(a-x)$ is replaced by $(a-\frac{1}{2}x)$ fairly concordant constants are obtained from all the experiments performed in aqueous hydrochloric acid. This modified equation, although empirical, may be derived from hypothetical considerations as follows: Assuming that the complex which mercuric chloride forms with hydrochloric acid in water solution is chiefly $H_2Hg_2Cl_6$ (and this assumption explains the phenomena observed in the cryoscopic and conductivity measurements, which Le Blanc and Noyes ascribe to the formation of the complex H_2HgCl_4) and that the reaction takes place essentially between the phosphorous acid and the single molecules of $HHgCl_3$ which are formed by the depolymerization of the double molecules $H_2Hg_2Cl_6$, it follows that the concentration of the molecules $HHgCl_3$ at any time t is not $(a-x)$ but $m(a-x)$, where m denotes that fraction of the total mercuric chloride present, at any time t, which is in the form of single molecules, $HHgCl_3$. Equation (5) may then be written:

$$\frac{dx}{dt} = km(a-x)\,(b-\tfrac{1}{2}x)\,(C+x), \qquad (7)$$

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* See K_1 in Tables III, IV, V and VI.

† According to LeBlanc and Noyes (Zeitschr. phys. Chem., vi, 329) mercuric chloride in the presence of aqueous hydrochloric acid forms complex compounds, such as $HHgCl_3.H_3HgCl_5$, H_2HgCl_4, $H_2Hg_2Cl_6$ and others more complex. They also found that the conductivity of normal hydrochloric acid is gradually depressed by 1·7 per cent if the solution is ¼ normal with respect to mercuric chloride, and by 17·9 per cent if the solution is normal with respect to mercuric chloride. This phenomenon they attribute partly to the extremely slow movement of the complexions and partly to their retarding effect on the hydrogen ions, and not to a lowering in the degrees of ionization of the complex compounds, since when mercuric chloride is mixed with aqueous hydrochloric acid in the proportion of $HgCl_2 : HCl$ the solution has the same catalytic effect upon the hydrolysis of methyl acetate as when the mercuric chloride is absent. This abnormal decrease in the conductivity may also be due to the fact that the equilibrium in the equation,

$$HHgCl_3 + HHgCl_3 \rightleftarrows H_2Hg_2Cl_6,$$

is shifted to the right with the increase in the concentration of the solution with respect to the mercuric chloride, and conversely. For further evidence in support of the assumption that the type of complex is $(HHgCl_3)_n$ and not H_2HgCl_4, see J. Sand and F. Breest, Zeitschr. phys. Chem., lix, 426 and lx, 237. Also Jander, Zeitschr. Electrochem., viii, 688.

where $$m = \frac{C_{HHgCl_3}}{C_{H_2Hg_2Cl_6} + C_{HHgCl_3}} \qquad \text{(a)}$$

From the Law of Mass Action,

$$H_2Hg_2Cl_6 \rightleftarrows HHgCl_3 + HHgCl_3,$$

whence $$\frac{C^2_{HHgCl_3}}{C_{H_2Hg_2Cl_6}} = k_1 \qquad \text{(b)}$$

and $$C_{HHgCl_3} = k_1^{\frac{1}{2}} C^{\frac{1}{2}}_{H_2Hg_2Cl_6} \qquad \text{(c)}$$

Substituting this value for C_{HHgCl_3} in equation (a)

$$m = k_1^{\frac{1}{2}} \frac{C^{\frac{1}{2}}_{H_2Hg_2Cl_6}}{C_{H_2Hg_2Cl_6} + C_{HHgCl_3}} \qquad \text{(d)}$$

If C_{HHgCl_3} at any time t is very small as compared with $C_{H_2Hg_2Cl_6}$, equation (d) may be changed to

$$m = k_1^{\frac{1}{2}} \frac{\left(C_{H_2Hg_2Cl_6} + C_{HHgCl_3}\right)^{\frac{1}{2}}}{C_{H_2Hg_2Cl_6} + C_{HHgCl_3}} \qquad \text{(e)}$$

$$m = k_1^{\frac{1}{2}} \left(C_{H_2Hg_2Cl_6} + C_{HHgCl_3}\right)^{-\frac{1}{2}} = k_1^{\frac{1}{2}} (a-x)^{-\frac{1}{2}} \qquad \text{(f)}$$

Substituting this value of m in equation (7)

$$\frac{dx}{dt} = kk_1^{\frac{1}{2}} (a-x)^{-\frac{1}{2}} (a-x) (b - \tfrac{1}{2}x)(C + x)$$

$$= kk_1^{\frac{1}{2}} (a-x)^{\frac{1}{2}} (b - \tfrac{1}{2}x)(C + x). \qquad (8)$$

In order to simplify equation (8) for integration, an approximate value for $(a-x)^{\frac{1}{2}}$ may be substituted :

$$(a-x)^{\frac{1}{2}} = a^{\frac{1}{2}} - \frac{1}{2(a)^{\frac{1}{2}}}x - \frac{1}{8(a)^{\frac{3}{2}}}x^2 - \frac{1}{16(a)^{\frac{5}{2}}}x^3 - \ldots$$

It is evident that all terms beyond the second decrease very rapidly, so that $(a-x)^{\frac{1}{2}}$ may be set equal approximately to

$$a^{\frac{1}{2}} - \frac{1}{2(a)^{\frac{1}{2}}}x = \frac{2a - x}{2(a)^{\frac{1}{2}}} = a^{-\frac{1}{2}}(a - \tfrac{1}{2}x).$$

Substituting this value in equation (8) and setting $k_1{}^{\frac{1}{2}}ka^{-\frac{1}{2}} = k_2$ we have,

$$\frac{dx}{dt} = k_2(a - \tfrac{1}{2}x)\,(b - \tfrac{1}{2}x)\,(\mathrm{C} + x), \qquad (9)$$

which is the equation sought.

This may be written

$$\frac{dx}{dt} = \frac{k_2}{4}(2a - x)\,(2b - x)\,(\mathrm{C} + x),$$

and, for convenience in integration, may be further simplified by setting $\frac{k_2}{4} = \mathrm{K}$; $2a = \mathrm{A}$ and $2b = \mathrm{B}$, gives:

$$\frac{dx}{dt} = \mathrm{K}(\mathrm{A} - x)\,(\mathrm{B} - x)\,(\mathrm{C} + x), \qquad (10)$$

whence

$$\mathrm{K} = \frac{2{\cdot}3}{(\mathrm{A} - \mathrm{B})\,(\mathrm{A} + \mathrm{C})\,(\mathrm{B} + \mathrm{C})t} \log \left(\frac{\mathrm{A} - x}{\mathrm{A}}\right)^{\mathrm{B+C}} \left(\frac{\mathrm{B}}{\mathrm{B} - x}\right)^{\mathrm{A+C}} \left(\frac{\mathrm{C} + x}{\mathrm{C}}\right)^{\mathrm{A-B}} \qquad (11)$$

If the amount of hydrochloric acid formed in the reactions is small as compared with the initial concentration of hydrochloric acid used, $\frac{\mathrm{C} + x}{\mathrm{C}}$ may be set equal to 1. Equation (10) then assumes the form

$$\frac{dx}{dt} = \mathrm{K}(\mathrm{A} - x)\,(\mathrm{B} - x), \text{ or}$$

$$\mathrm{K} = \frac{2{\cdot}3}{(\mathrm{A} - \mathrm{B})t} \log \frac{(\mathrm{A} - x)\mathrm{B}}{(\mathrm{B} - x)\mathrm{A}} \qquad (12)$$

EXPERIMENTAL. *Standardization of the Mercuric Chloride and the Phosphorous Acid.*

The desired amount of mercuric chloride was dissolved in distilled water or in aqueous hydrochloric acid of known concentration. Of this solution 10^{cm^3} were pipetted off, by means of a carefully calibrated pipette, and transferred into several glass test tubes of about 40^{cm^3} capacity which had previously been constricted at about 1½ inches from the mouth to a size just large enough to admit the stem of the pipette and to allow the displaced air to escape. To this were added 10^{cm^3} of a solution containing about 1½ times the theoretical amount of phosphorous acid. The tubes were then sealed, allowed to cool, the contents well mixed, and the tubes submerged in a thermostat kept at 60°. When two consecutive analyses of the mercurous chloride in the tubes about twenty-four hours apart showed no increase or decrease in the amount of the mercurous chloride the reduction was considered complete. Moreover, these results always agreed, within 0·1 to 0·05 per cent, with the theoretical amount of mercurous chloride calculated from the mercuric chloride originally present. In a similar manner the concentration of the phosphorous acid* was determined by using an excess of mercuric chloride.

Reaction Velocity Measurements.—All the experiments were carried out in sealed glass test tubes. As soon as two tubes were filled with 10^{cm^3} of the standardized mercuric chloride and 10^{cm^3} of the standardized phosphorous acid, they were sealed, allowed to cool, shaken and submerged in a thermostat, where they were held in position by means of coiled brass springs. In the case of the experiments carried out at 25° the time t was counted from the moment the tube was submerged until it was removed from the thermostat, while in the experiments at 60° two minutes were allowed for each tube to assume the temperature of the water of the thermostat. At definite intervals a tube was withdrawn, three scratches made with a sharp triangular file in a horizontal plane, on each side of which was placed a folded piece of wet filter paper. The tube was then brought in a vertical position to the point of a small blast lamp flame, care being taken not to allow the upper part of the tube to fly off, as it often contained some mercurous chloride. After the tube was thus cracked the upper part was lifted off and the contents filtered and washed (until the wash water was free from chlorine) through an ignited and weighed perforated platinum crucible, fitted with an asbestos mat. After most of the moisture had been exhausted by the aspirator the crucible was suspended in a glass weighing bottle and placed in a drying oven at a temperature of about 80°. The temperature was then gradually raised to 105° and maintained between 105° and 110° for thirty minutes.

It is well known that mercurous chloride at that temperature is apt to suffer a slight loss due to volatilization. This loss, however, is almost entirely avoided, first, by drying the mercurous chloride for about 15 minutes by means of the aspirator, secondly by raising the temperature gradually in order to avoid the rapid formation of steam, which is apt to carry some of the mercurous chloride with it. Furthermore, the mercurous chloride, being precipitated in this reaction in crys-

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* Of a number of samples of phosphorous acid tested, only one, that furnished by J. T. Baker Co., proved sufficiently pure. This consisted of a 25 per cent solution, 96 per cent of its total acidity being phosphorous acid.

talline form, probably has a lower vapor pressure than the ordinary amorphous form. Great care must also be exercised in cracking off the top of the test tube, as the latter if not uniformly handled during the constriction and sealing is apt to splinter.

It was found advisable in filtering the mercurous chloride to use light suction at first to avoid clogging of the asbestos mat, which would vitiate the experiment because of the delay in stopping the reaction. After practice it was found possible to accomplish the separation of the precipitate from the solution in about one minute (exclusive of washing). In the experiments at 60° this time factor is of course of importance.

Experimental Results.

The catalytic effect of hydrochloric acid in the reduction of mercuric chloride by phosphorous acid at 60° is shown in the graph on the following page and at 25° opposite p. 365. The weights of mercurous chloride, five milligrams to the millimeter, are expressed as ordinates; and the time, two minutes to the millimeter in fig. I, and one hour to the millimeter in fig. II, are expressed as abscissas.

Table III.

$HgCl_2$ = 0·132 gram mols per liter $= a$
H_3PO_3 = 0·0575 " " " " $= b$ $T = 60°$
HCl = 0·264 " " " " $= C$

t	$x = HgCl$			
in min.	in grams	in mols	K_1*	K_2†
24	0·1462	0·03104	0·406	0·189
59	0·2880	0·06115	0·453	0·188
93	0·3750	0·07962	0·510	0·189
152	0·4578	0·09720	0·616	0·189
186	0·4848	0·10293	0·684	0·190
228	0·5068	0·10760	0·778	0·191
∞	0·5417	0·11500		

* Calculated from Equation (6). † Calculated from Equation (11).

$HgCl_2$ = 0·132 gram mols per liter $= a$
H_3PO_3 = 0·0575 " " " " $= b$ $T = 60°$
HCl = 0·132 " " " " $= C$

t	$x = HgCl$			
in min.	in grams	in mols	K_1*	K_2†
27	0·0964	0·02047	0·419	0·200
59	0·1928	0·04094	0·443	0·200
154	0·3820	0·08110	0·557	0·206
274	0·4848	0·10293	0·758	0·214
360	0·5132	0·10896	0·893	0·214
∞	0·5417	0·11500		

* Calculated from Equation (6). † Calculated from Equation (11).

FIG. I.

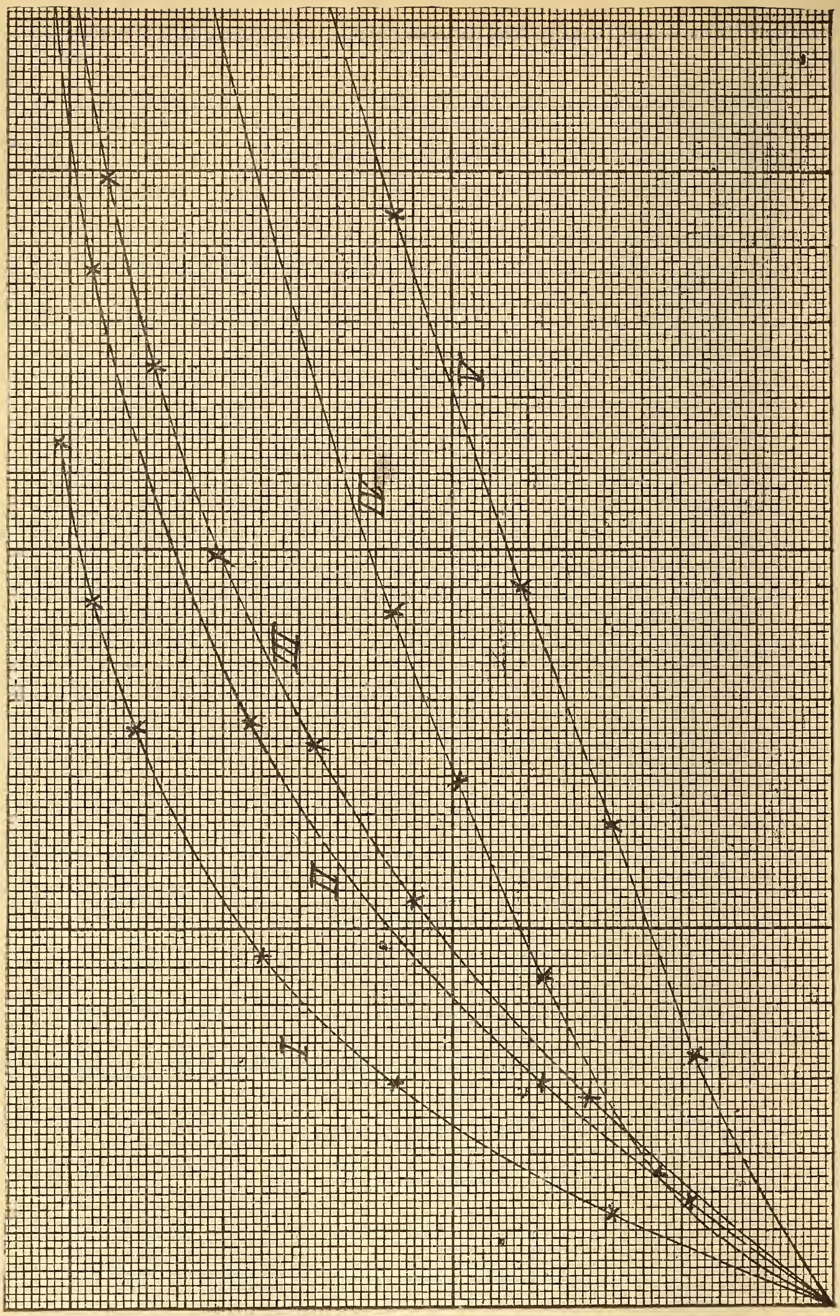

Fig. I {
Curve I represents the experiment performed in 0·264N HCl
" II " " " " " 0·132N HCl
" III " " " " " 0·1N HCl
" IV " " " " " water solution
" V " " " " " 0·264N NaCl*

* The results of this experiment will be discussed in a subsequent paper.

TABLE III (continued).

$HgCl_2$ = 0·132 gram mols per liter = *a*
H_3PO_3 = 0·0575 " " " " = *b* T = 60°
HCl = 0·1 " " " " = C

t	x = HgCl			
in min.	in grams	in mols	K_1*	K_2†
55	0·1610	0·03418	0·479	0·221
107	0·2746	0·05830	0·536	0·218
148	0·3406	0·07231	0·536	0·215
198	0·4060	0·08620	0·620	0·221
248	0·4456	0·09461	0·671	0·219
298	0·4754	0·10093	0·741	0·221
358	0·4991	0·10597	0·833	0·221
418	0·5144	0·10921	0·923	0·223
∝	0·5417	0·11500		

* Calculated from Equation (6). † Calculated from Equation (11).

TABLE IV.

$HgCl_2$ = 0·132 gram mols per liter = *a*
H_3PO_3 = 0·0585 " " " " = *b* T = 25·2°
HCl = 2·0 " " " "

t	x = HgCl			
in hrs.	in grams	in mols	K_1*	K_2†
5·1	0·1446	0·0307	0·518	0·241
8·3	0·2100	0·0446	0·543	0·241
10·0	0·2392	0·0508	0·557	0·241
13·1	0·2840	0·0603	0·580	0·241
15·5	0·3104	0·0659	0·587	0·236
23·8	0·3820	0·0811	0·629	0·235
31·0	0·4198	0·0891	0·728	0·224
∝	0·5511	0·1170		

* Calculated from Equation (4). † Calculated from Equation (12).

$HgCl_2$ = 0·132 gram mols per liter = *a*
H_3PO_3 = 0·0585 " " " " = *b* T = 25·2°
HCl = 1·0 " " " "

t	x = HgCl			
in hrs.	in grams	in mols	K_1*	K_2†
7·0	0·1290	0·0274	0·325	0·153
10·3	0·1760	0·0374	0·336	0·153
14·4	0·2246	0·0477	0·348	0·153
24·0	0·3130	0·0665	0·386	0·156
31·5	0·3600	0·0764	0·409	0·155
49·8	0·4342	0·0922	0·471	0·153
57·5	0·4544	0·0965	0·500	0·152
73·5	0·4830	0·1026	0·538	0·149
∝	0·5511	0·1170		

* Calculated from Equation (4). † Calculated from Equation (12).

Fig. II.

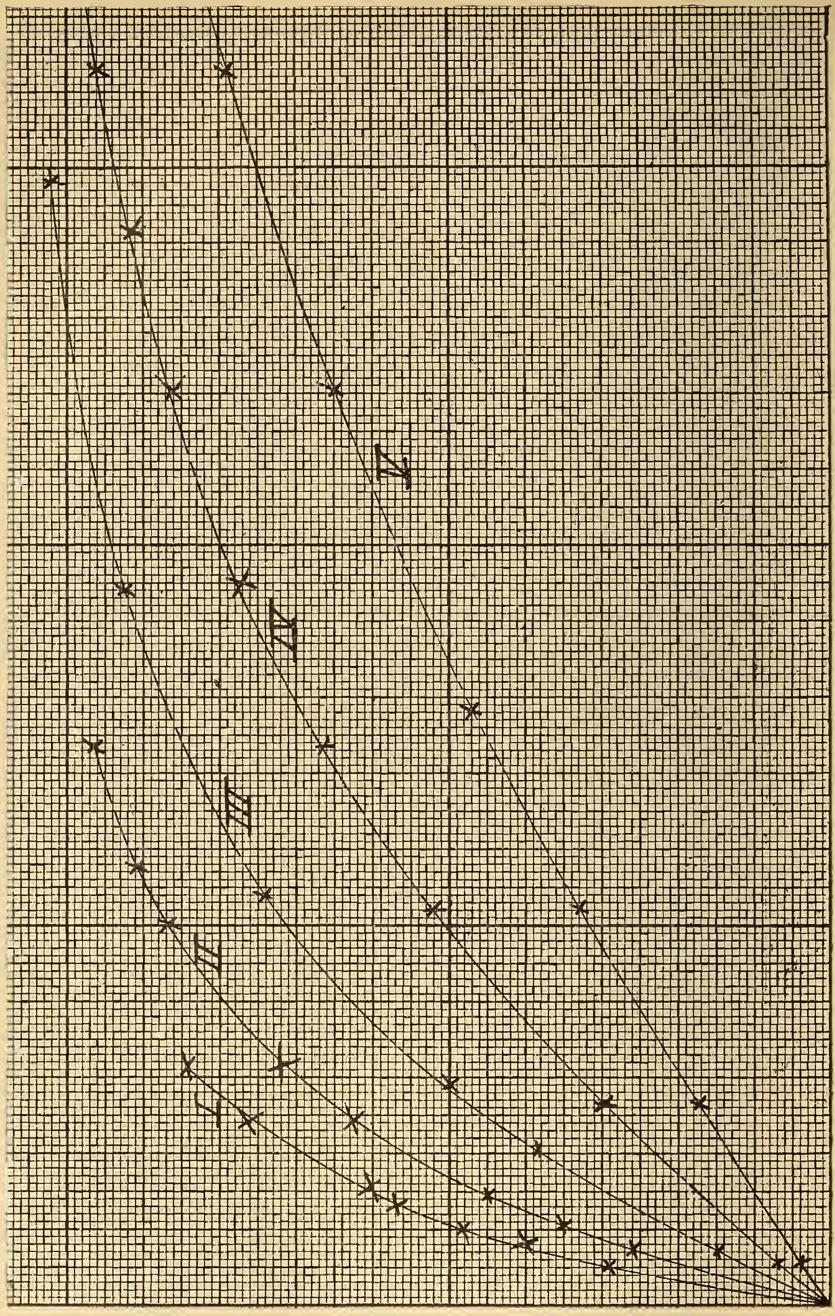

Fig. II
Curve I represents the experiment performed in 2N HCl
" II " " " " " 1N HCl
" III " " " " " 0·5N HCl
" IV " " " " " 0·264N HCl
" V " " " " " 0·132N HCl

TABLE IV (continued).

$HgCl_2$ = 0·132 gram mols per liter = a
H_3PO_3 = 0·059 " " " " = b T = 25·2°
HCl = 0·5 " " " " = C

t	$x = \text{HgCl}$			
in hrs.	in grams	in mols	K_1*	K_2†
6·9	0·0754	0·01601	0·336	0·163
20·5	0·1936	0·04110	0·367	0·166
29·0	0·2510	0·05329	0·388	0·167
54·2	0·3704	0·07864	0·458	0·171
94·0	0·4626	0·09822	0·563	0·170
148·0	0·5122	0·10875	0·664	0·161
∝	0·5558	0·11800		

* Calculated from Equation (6). † Calculated from Equation (11).

$HgCl_2$ = 0·132 gram mols per liter = a
H_3PO_3 = 0·059 " " " " = b T = 25·2°
HCl = 0·264 " " " " = C

t	$x = \text{HgCl}$			
in hrs.	in grams	in mols	K_1*	K_2†
5·7	0·0356	0·00756	0·339	0·167
26·3	0·1500	0·03185	0·371	0·173
52·0	0·2606	0·05554	0·417	0·178
73·7	0·3322	0·07053	0·460	0·183
95·0	0·3840	0·08153	0·504	0·185
120·3	0·4304	0·09138	0·563	0·189
141·6	0·4582	0·09728	0·610	0·189
163·2	0·4792	0·10174	0·656	0·189
214·0	0·5110	0·10849	0·756	0·187
261·5	0·5266	0·11180	0·809	0·182
∝	0·5558	0·11800		

* Calculated from Equation (6). † Calculated from Equation (11).

$HgCl_2$ = 0·132 gram mols per liter = a
H_3PO_3 = 0·059 " " " " = b T = 25·2°
HCl = 0·132 " " " " = C

t	$x = \text{HgCl}$			
in hrs.	in grams	in mols	K_1*	K_2†
5·7	0·0198	0·00420	0·366	0·181
26·5	0·0884	0·01877	0·378	0·181
52·0	0·1652	0·03507	0·398	0·184
78·2	0·2350	0·04989	0·428	0·188
120·3	0·3254	0·06909	0·478	0·192
163·0	0·3940	0·08365	0·540	0·197
214·0	0·4500	0·09554	0·627	0·202
261·3	0·4838	0·10272	0·709	0·204
308·0	0·5060	0·10743	0·789	0·205
∝	0·5558	0·11800		

* Calculated from Equation (6). † Calculated from Equation (11).

TABLE V.

$HgCl_2$ = 0·132 gram mols per liter = *a*
H_3PO_3 = 0·067 “ “ “ “ = *b* T = 25·2°
HCl = 1·0 “ “ “ “

t	*x* = HgCl			
in hrs.	in grams	in mols	K_1*	K_2†
5·6	0·1186	0·0252	0·314	0·148
10·0	0·1936	0·0411	0·337	0·151
24·6	0·3558	0·0755	0·401	0·153
33·0	0·4114	0·0837	0·435	0·152
47·5	0·4752	0·1009	0·500	0·148
56·5	0·5006	0·1063	0·530	0·145
80·0	0·5414	0·1150	0·600	(0·134)
∞	0·6217	0·1320		

*Calculated from Equation (4). †Calculated from Equation (12).

$HgCl_2$ = 0.132 gram mols per liter = *a*
H_3PO_3 = 0·067 “ “ “ “ = *b* T = 25·2°
HCl = 0·5 “ “ “ “ = C

t	*x* = HgCl			
in hrs.	in grams	in mols	K_1*	K_2†
6·3	0·0794	0·01686	0·342	0·167
22·2	0·2356	0·05000	0·388	0·171
32·0	0·3064	0·06505	0·417	0·173
48·2	0·3930	0·08344	0·474	0·175
93·7	0·5166	0·10968	0·650	0·170
141·0	0·5634	0·11962	0·799	(0·154)
∞	0·6217	0·13200		

*Calculated from Equation (6). †Calculated from Equation (11).

$HgCl_2$ = 0·132 gram mols per liter = *a*
H_3PO_3 = 0·067 “ “ “ “ = *b* T = 25·2°
HCl = 0·264 “ “ “ “ = C

t	*x* = HgCl			
in hrs.	in grams	in mols	K_1*	K_2†
6·3	0·0468	0·00994	0·359	0·179
22·4	0·1512	0 03210	0·379	0·180
31·8	0·2056	0·04365	0·401	0·184
48·2	0·2860	0·06072	0·437	0·189
93·2	0·4370	0·09278	0·570	0·195
194·0	0·5614	0·11920	0·931	0·196
∞	0·6217	0·13200		

*Calculated from Equation (6). †Calculated from Equation (11).

TABLE VI.

$HgCl_2$ = 0·134 gram mols per liter = $2a$
H_3PO_3 = 0·067 " " " " = a T = 25·2°
HCl = 1·0 " " " "

t in hrs.	x = HgCl in grams	x = HgCl in mols	K_1*	K_2†
8·8	0·1724	0·0366	0·159	0·146
21·6	0·3280	0·0694	0·185	0·149
29·8	0·3910	0·0830	0·204	0·149
48·0	0·4782	0·1015	0·242	0·147
54·3	0·4968	0·1055	0·254	0·144
∞	0·6311	0·1340		

* $\frac{dx}{dt} = k\,(2a - x)\;(a - \frac{1}{2}x) = \frac{1}{2}k\,(2a - x)\;(2a - x) = K_1\,(2a - x)^2$, whence $K_1 = \frac{x}{2a\,(2a - x)\,t}$ (see Equation (1)).

† Calculated from Equation (12).

Summary.

1. By Ostwald's "method of isolation" it is shown that the reaction between mercuric chloride and phosphorous acid is of the first order with respect to the mercuric chloride.

2. The total reaction is of the second order and takes place in two stages, probably the following:

$$\text{(a)}\quad HgCl_2 + H_3PO_3 = HCl + HgCl + H_2PO_3$$
$$\text{(b)}\quad 2H_2PO_3 + H_2O = H_3PO_3 + H_3PO_4,$$

reaction (b) being fairly rapid as compared with reaction (a) so that the concentration of the H_3PO_3 at any time t may be denoted approximately by $(b - \frac{1}{2}x)$ instead of $(b - x)$, since for every two molecules of H_3PO_3 decomposed one molecule of H_3PO_3 is regenerated.

3. Conclusive evidence is presented that the reaction is accelerated by hydrogen ions.

4. If no hydrochloric acid is present at the outset, the velocity coefficient K, calculated for a reaction of the second order, goes through a minimum. This may be due partly to the initial rate of the secondary reaction gradually increasing with increase of the hydrogen ions, but is chiefly due to the formation of complexes between the $HgCl_2$ and the HCl formed in the reaction, and to their subsequent decomposition with decrease in concentration of the mercuric chloride.

5. When hydrochloric acid is present at the outset the velocity coefficient, calculated for a reaction of the second order, shows a steady increase to two or three times its initial value. This, however, is what would be expected, on account of the breaking down of the complexes with decreasing concentration, upon the assumption that only the single molecules of $HHgCl_3$ react with phosphorous acid.

6. Fairly concordant velocity constants are obtained if, in the velocity equation (5), $(a-x)$ is replaced by $m(a-x)$, where m denotes that fraction of the total mercuric chloride present, at any time t, which is in the form of single molecules ($HHgCl_3$), whose concentration is assumed to be always small in comparison with that of the double molecules, $H_3Hg_2Cl_6$.

Art. XXXIII.—*Sky Radiation and the Isothermal Layer;*

by Frank W. Very.

Introductory.

During the hours of sunshine, light from the sky, and to a smaller extent invisible infra-red radiation from the same source, fall upon the earth's surface in addition to the direct rays of the sun. This secondary source of modified sunlight, diffused by the air and its floating dust, constitutes during most of the day only a fraction of the total radiation received. The heat communicated to the earth's surface by this incoming radiation makes the earth a source of infra-red radiation of extreme wave-length; but since of the two sources of supply that from the sky is much the smaller, the incoming radiation from the sky is less than the outgoing radiation to the sky which has been derived from the total heat due to the combined primary and secondary sources. Consequently, the sky behaves like a cold body by day as well as by night, its effective temperature may be measured, and something may be learned from the phenomena of sky radiation in regard to the constitution of the earth's atmosphere and the processes by which the earth parts with the radiation which it receives from the sun.

General Phenomena of Atmospheric Radiation.

In the experiments described in my treatise on "Atmospheric Radiation,"* I found that some of the more absorbent vapors are incapable of direct radiation through a distance of more than a few centimeters. It follows that the aqueous vapor and carbon dioxide of the lower atmospheric layers can not radiate directly to space notwithstanding their great radiant power.

But in addition to this, the more transparent gases, the oxygen and nitrogen of the air, are opaque to their own radiations in layers of some meters thickness and cannot radiate to outer space by the direct way until the limit of altitude for these gases is approached, where the remaining material is insufficient to produce complete absorption. The depths of the layer beyond which direct radiation ceases will vary, not only for the different constituents of the atmosphere, but also for different radiant lines in the spectrum of the same gas or vapor. Each emission line in a spectrum has a different coefficient of absorption by subsequent layers of the emitting gas. Some lines are of such feeble intensity that a depth of many miles of

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* Bulletin G, U. S. Weather Bureau, 1900.

the absorbent may be needed to give them sensible strength, and such lines may be radiated from depths which are approximately equal to the entire atmosphere, but other lines are so intense that they are absorbed by the substance in exceedingly attenuated form and by very thin layers. Many of the lines and bands of aqueous vapor are of this character.

Now the distribution of vapor in the atmosphere is conditioned by temperature, and as long as there remains a quantity of even the less absorbent gases sufficient to preserve a temperature above the point at which vaporization can take place, vapors of the more condensible substances will continue to be found. It is not necessary that the temperature shall be above the melting point of the substance. Ice vaporizes at temperatures far below the freezing point. Carbon dioxide is an example of a substance which vaporizes directly from the solid state without previous melting, even when heat is applied.

Some vapors, and notably that of water, have extraordinary powers of radiant absorption. At a temperature of −30° C., when the surface air contains less than 0·3 gram per cubic meter of aqueous vapor, I found that the great Ξ band in the solar spectrum still produced an almost complete extinction of the spectrum between 5 μ and 8 μ. In the upper isothermal layer where the temperature falls to −60° Centigrade, the aqueous vapor is reduced to about one-tenth of the above quantity, but there are many kilometers of air at this nearly constant temperature, and sometimes with a relative humidity as high as 50 per cent up to 25 kilometers.* Thus the total depth of absorbent vapor is by no means inconsiderable in this extensive upper layer, and the intensity of the great Ξ band is so extraordinary that it will continue to be a feature of the infra-red spectrum at these extreme elevations. Here also the atmosphere first begins to part with a portion of its heat by radiation to outer space.

The Loci of Terrestrial Radiation.

There are three principal loci of terrestrial radiation, namely: (1) A thin heated superficial layer of the terraqueous globe; (2) the solid or liquid particles suspended in the air, constituting haze, smoke, or cloud; and (3) the upper static layer of tem-

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* See W. R. Blair, "Free Air Data," Bulletin of the Mount Weather Observatory, vol. 4, part 4, 1912.

For example :	Sept. 11, 1910,	Rel. humidity =	56%	at	24899^{m}	(p. 245).
	Sept. 13, 1910,	" "	69	"	17258	(p. 247).
	Feb. 16, 1911,	" "	60	"	14248	(p. 258).
	March 3, 1911,	" "	50	"	19050	(p. 270).
	March 4, 1911,	" "	55	"	17575	(p. 271).

perature-inversion, a layer many kilometers deep, which is truly the radiant layer of the atmosphere.

The radiation from the first sources forms a continuous spectrum, but that from the third, or atmospheric source, is discontinuous. The absorption of solar rays by the upper layers of the atmosphere is not only the cause of the extra heat in the layer of permanent temperature-inversion, but variations in the distribution of absorbent ingredients within the layer also occur and are accompanied by simultaneous fluctuations of temperature. Thus this region is only approximately "isothermal," and is so more especially on account of the very slow change in its vertical temperature-gradient as compared with the steep gradients of the lower air, and from its seasonal constancy.

"The greatest changes of temperature noted from one observation to the next," says Mr. W. R. Blair,* "all levels considered, take place at the surface of minimum temperature" at an altitude of about 17 km. This observation by the staff of the Mount Weather Observatory confirms the supposition on p. 123 of my work on "Atmospheric Radiation" that the elevated regions of the atmosphere up to at least 20 km. undergo much larger temperature variations than the more deeply situated layers of the free air owing to the larger incipient absorption of the incoming solar rays by the moisture in the upper air. The altitude of 20 km. assumed in my former publication as an approximate limit of the aqueous atmosphere within which thermal conservation is produced through absorption of solar radiation by aqueous vapor, was derived from a preliminary charting which I made of some of Glaisher's observations, and must be extended perhaps to about the same height as the atmosphere of oxygen or nitrogen. A measurable amount of aqueous vapor is still found at 30 km.

The lowering of the level of the more potent aqueous absorption in descending air movements gives temperature-maxima at the level of greatest temperature variation (about 17 km.); and conversely, ascending movements bring minimum temperatures at this point, because the level of maximum thermal increment through incipient absorption has been elevated, while at the same time locally transported air has been cooled by expansion. Temperature-inversions associated with bodies of especially moist or especially absorbent (that is, nearly moisture-saturated) masses of air occur at all levels, but are sometimes most marked at an elevation of 2000 or 3000 meters during strong descending movements of the atmosphere, the two causes (namely, lowering of the level of incipient absorption, and presence of

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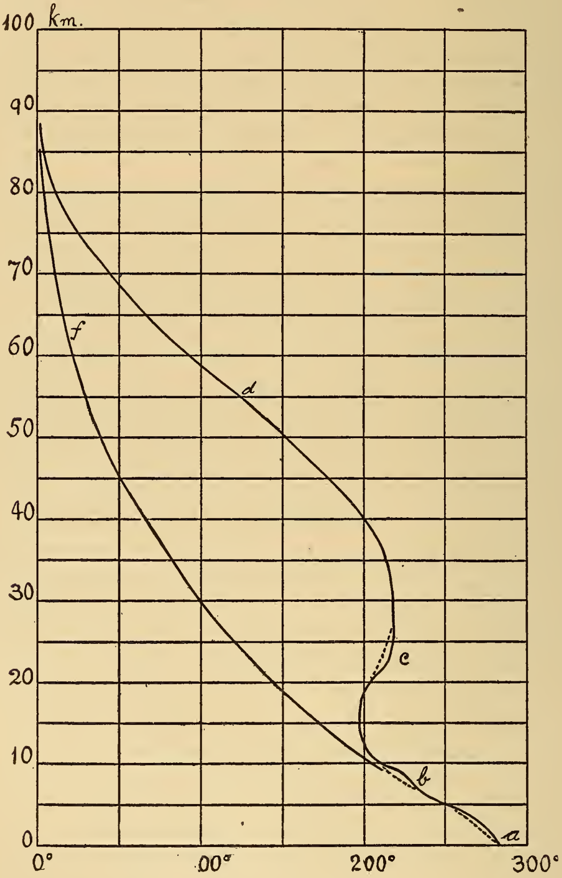
* Bulletin Mount Weather Observatory, vol. iv, p. 203, 1912.

an especially absorbent layer) here coinciding to reinforce the phenomenon.*

If the curve of absolute temperature between the surface and an altitude of 10 km. be extended by estimate so that it becomes asymptotic to the axis of altitude at 100 km. for absolute zero,† we get the curve *a f* of fig. 1, and a similar extension of the curve of observation (which is already known up to 30 km., or just past the maximum of the inverted layer) gives

Fig. 1.



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* For examples, see the temperature-inversions recorded by W. R. Blair in the Bulletin of the Mount Weather Observatory, vol. iv, part 5, observations of September 22d and 30th, 1911, pp. 379 and 383, also Chart No. xviii.

† The outer layers of hydrogen and other light gases will extend this curve to greater altitudes, but we have not enough information to warrant the extension at present.

a b c d. The area between the two curves represents heat communicated to the air through the absorption of solar radiation. The slight upward convexity at *a* is due partly to heat from absorption of terrestrial radiation and partly to condensation of moisture in the lower air. Local and temporary irregularities, as at *b* and *c*, indicate upper regions of aqueous condensation. In region *a*, the nuclei which serve as centers of aqueous condensation are mainly dust particles carried up from the surface in the local convection, as Aitken has demonstrated. At the higher condensation levels, since the relative humidity is not often above 55 per cent, Blair suggests that the condensation may be produced around nuclei of carbonic acid (H_2CO_3) which, though unstable at ordinary temperatures, appear to exist at the temperature of the upper isothermal layer. To some extent volcanic and cosmic dust furnishes condensation nuclei at very great altitudes, where luminous night-clouds are sometimes seen. The heat communicated to the air by aqueous condensation is greatest in the lower and moister layers, yet even here this source is of small account compared with the great accession of heat from the sun's rays in the upper air.

Professor W. J. Humphreys* has published his opinion that my explanation of the isothermal layer is incorrect because "the water vapor is not there to absorb."† He accepts the conclusion that the heat comes from the absorption of radiation, but assigns the absorption to "oxygen and ozone."‡ The first proposition, that water vapor is lacking, is disproved by the U. S. Weather Bureau observations already cited. By spectro-bolometric observations it can be shown that the ozone bands "in the infra-red, one of which, 8·5 μ to 10·5 μ, is very strong, and of course would absorb earth radiations," § occur actually in that part of the infra-red spectrum which would otherwise be most readily transmitted to space, and where the telluric radiation should also attain its maximum strength according to Wien's law. Knut Ångström,‖ who first assigned their origin to these bands, gives the limits of greatest absorption "from $\lambda = 9{\cdot}1\ \mu$ to $\lambda = 10{\cdot}0\ \mu$." I have observed them on several occasions in the solar spectrum, but not always with certainty in the lunar spectrum, where, however, some allowance must be made for the difficulty of the observation. Ozone has always been regarded as one of the most variable constituents of the atmosphere. If its regular diurnal production in the upper air by the action of the sun's ultra-violet rays is conceded, the

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* Astrophysical Journal, vol. xxix, p. 14, January, 1909.

† Op. cit., p. 22. ‡ Op. cit., p. 29. § Op. cit., p. 28.

‖ "Die Ozon-bänder des Sonnenspektrums und die Bedeutung derselben für die Ausstrahlung der Erde," Arkiv för Matematik, Astronomi och Fysik, i, p. 395, 1904.

ozone must still suffer a corresponding destruction both by day and by night through union with aqueous vapor to make hydrogen peroxide. Traces of H_2O_2 in rain water are greater by day than by night, which lends support to the supposition that there is increased formation of the peroxide in the daylight hours. The production of H_2O_2 by the sun's rays has also been verified experimentally by Kernbaum.* But granting the existence of a considerable quantity of ozone as a permanent constituent of the upper air, and that this substance must be included among the leading absorbents of telluric radiation, taking its place with aqueous vapor and carbon dioxide, and supplementing these substances in a region of the spectrum where they are least effective, nevertheless ozone does not appear to be the cause of the isothermal layer, for it contributes very little to the absorption of solar rays, while, on the contrary, the absorption bands of aqueous vapor invade regions of the spectrum where the solar rays have considerable power, and finally the hydrols are potent near the very maximum of the energy in the solar spectrum.

The altitude at which the lowest limit of the isothermal layer begins is determined by the amount of material in the lower air suitable for absorbing terrestrial radiation and on the intensity of this absorption. The commencement of the isothermal layer is several thousand meters higher in the tropics than in Europe, because the greater humidity of the tropical air makes it a conservator of the atmospheric radiant potential up to an altitude of about 15,000^m, as compared with 10,000 to 12,000^m for the less moist air of the higher latitudes. On account of its greater average elevation, the tropical isothermal layer has a smaller average density, a smaller mass per unit of section, and it absorbs less of the solar radiation. Hence its temperature is a little lower than in Europe, since the accumulating power of the layer is greatly aided by its enormous depth, and a lessening of the depth by several kilometers can not but have an appreciable effect.

Blair† inclines to the conclusion that, "in general, the peculiarities in the temperature gradient up to and including the upper or permanent inversion owe their existence to the influence of convection on the distribution of the constituents, especially of the water of the atmosphere." Clayton, however, attributes "a sudden fall of temperature which occurs after sunrise (about 9 A. M. in summer)" at a height of about 1000 meters, to the cooling by expansion of ascending bodies of air, forming part of the low-level convection system, and carried upward by their momentum beyond the point of equilibrium.‡ This

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* Bulletin Internat. Akad. Sci. Cracovie, 1911, p. 583. † Op. cit., p. 212.

‡ "The Diurnal and Annual Periods of Temperature," etc., Annals Harvard Observatory, vol. lviii, part 1, p. 18-19, 1904.

explanation limits local convection to a superficial layer about 1500 meters deep within which the ordinary fair-weather cumuli originate. Temperature variations, both diurnal and annual, continue, however, above this point. The range of temperature at 8000 meters is over 50 per cent of that at the surface, and variations of 18° C. on dates only a few days apart are found at an altitude of 17,000 meters.

Irregularities in the distribution of the chief absorbents of radiation in the atmosphere, which are aqueous vapor and its products, the hydrols, are certainly responsible for most of the atmospheric thermal variations, and if the term "convection" be extended to include not only the process of thermal exchange between the earth's surface and the first cumulus level (which is the sense in which Clayton employs the word in the passage cited), but also the wider cyclonic and planetary circulation, we may accept Blair's statement, understanding by this a convectional process by which warm, moist air is carried upward from the earth's surface, or by secondary convection from local cloud layers, or on a larger scale in a planetary circulation where moist air, starting from the earth's surface in the tropics, travels polewards, gaining both easting and altitude as the latitude increases.

Convection, in the sense of an overturning of gravitational equilibrium, has practically ceased in the upper layer of temperature-inversion; but persistence of momentum carries some part of the poleward planetary circulation into this elevated region, thereby continually replenishing it with sufficient moisture to serve as a potent absorbent of the solar rays within the limits of the numerous and broad aqueous bands of the infra-red spectrum, and at times bringing an unusual accession of vapor. Here is the main source of occasional exceptional heat in the upper inversion layer. Nevertheless, the *constancy* of this layer throughout the globe differentiates it immediately from an effect of the ever-varying winds, and the sudden increase in the second differential of the thermal energy transferred from layer to layer on entering this region, marks the process by which the isothermal layer originates as a radiant one. Here, and here only, can there be any direct radiation of the atmosphere to space. The radiant process does indeed exist at all levels in the atmosphere, but in the lower air it is an indirect successive alternation of radiation and absorption of radiation by innumerable steps—a mode of communication more rapid than that by penetration through local molecular motion, but still one which is slow compared with the velocity of radiation.*

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* Compare the account of this step-by-step process of atmospheric radiation which is given in my work on "Atmospheric Radiation," pages 114-115 and 124.

Blair suggests tentatively that the midday depression of temperature at 3000 meters is due to the diminished transmission of telluric radiation by the lower air at this time on account of the dust and aqueous vapor carried upward in the local convection, and that the maximum at 3^h A. M. at the same level is caused by the nocturnal settling of dust and moisture which clears the air and renders it more transmissive. A diurnal variation in the transmissive quality of the atmosphere is certain, but whether it is competent to produce as wide a fluctuation of temperature as the one at 3000^m with a total range of 3·7° C. and with the supposed lag in the phase, can not yet be proved. Clayton's hypothesis accounts for the facts very well, and I find little evidence of any marked difference in the escape of telluric heat by radiation to the zenithal sky in the daytime as compared with night, or at least the variations which are observed are capable of simple explanation in changing cloudiness.

OBSERVATIONS OF SKY RADIATION.

During many years I have made occasional observations of the radiation of a blackened bolometer or thermopile to the sky. Perfectly pure skies are rare, and increasingly so in the neighborhood of our large cities.* A transcript of all of the measurements would therefore have little interest, as it would record mainly the imperfections of the sky. Nevertheless, such observations do tell us something in regard to the nature of the atmospheric radiant processes. The experiments were made with the heat-measuring apparatus pointing to a plane metallic mirror reflecting to the sky, or to the ground, or to a black card at air temperature.

If the absorption of telluric radiation by the atmosphere were complete, there would be no radiation to the sky. This happens, indeed, when the sky is completely cloudy. But actually, with a clear sky and normal vapor content, there are extensive regions of the infra-red spectrum which pass readily through the air, as the infra-red spectrum of the moon demonstrates. These spectral regions of ready transmissibility are but little affected in the following measures by any changes in the vaporous contents of the atmosphere, except in one case of a supersaturated air layer which will be specially noted.

The effective temperature of the radiating earth in consequence of the somewhat free transmission of its radiation to space is not the mean temperature of the cool air at a considerable elevation above the surface, but depends largely upon the temperature of the surface of the ground, which is much

* My present situation is 12 miles from the center of Boston.

greater than that of the entire air column. Moreover, the temperature of the air, with its clouds and aqueous vapor from which its own radiation partly proceeds, is not purely obtained by radiation exchanges, but is due to a complex of radiation, convection, absorption, cloud precipitation, etc.

The radiation absorbed by the aqueous vapor of the lower air is not re-radiated directly into space, for it can not pass the barrier of aqueous vapor at higher levels, but this thermal energy is passed on to other atmospheric constituents, to the dust, or to the major part of the air, its oxygen and nitrogen, which, though feeble radiators, must be the final members of the series by which the heat of the atmosphere is dispersed into space.

The day temperature of sunlit rock, gravel, dry sand, or moderately dry soil is much higher than the air temperature at a height of one meter, or thereabouts, which is set down in the usual meteorological data as the observed terrestrial temperature. Thus a surface temperature of 120° F. for the first half centimeter of dry soil is common in summer when the air temperature is nearer 75° or 80° F., and the mean temperature of land surfaces for day and night has been quite generally assumed too low from neglecting this sunshine effect. With the low sun of winter in the following measures, the sunshine effect is of little consequence, and the ground measures were always of a shaded surface. The radiator in these observations has been the measuring instrument itself, kept at a nearly constant temperature of about +60° F. throughout the winter series. In order that there may be the means of computing the radiation of the soil to the atmosphere, measures of the radiation of the instrument towards the ground have also been included.

The temperature of the ground when frozen and partly covered with ice was assumed to be the same as that of the air one meter above the surface; but when the ground was covered with snow, the surface temperature was taken by a thermometer with its bulb barely covered by the snow. Usually there is scarcely any difference between the temperature of the shaded surface and that of the air in the daytime, nor yet at night if the sky is veiled by even the thinnest cloud. But on the morning of February 4th, 1909, an exception was noted which is of sufficient interest to be recorded.

At $5^h\ 15^m$ A. M., the sky being covered by cirro-stratus cloud dense enough to give a strong lunar halo and corona, the snow had a temperature of −6·0° F., but the air, which was calm, was at 0° F. I was surprised at the magnitude of the temperature depression, which seemed too great to be produced by nocturnal radiation to such a cloudy sky. The explanation appeared presently, for at $6^h\ 30^m$ A. M., over an hour later, the air temperature by a fan-ventilated instrument one meter above the surface was +3·0° F., dew-point = +2·0°, relative humidity = 0·94, while the snow remained at −6·0° F., or the depression had increased to −9°. In still another hour, at $7^h\ 35^m$ A. M., the sun had risen, the sky remained as before, the air temperature was +2·2° F., relative humidity = 100 per cent, but the shaded snow on the west side of the building, and about 5 meters from it and freely exposed to the sky, remained as before at precisely −6·0° F. *The air was perfectly calm.* A dense fog had formed in the Neponset valley, but did not reach our level. Soon after this, a gentle breeze sprang up and the snow rapidly assumed the same temperature as the air.

It is evident that during the whole of the earlier observations, a thin layer of supersaturated air adhered to the surface of the snow. The radiant absorption by air supersaturated with moisture is extraordinarily great, and, in this case, it prevented the snow from receiving radiation, while downward conduction from the slightly warmer air at one meter was insignificant, and thus the snow retained the temperature which had been given to it by nocturnal radiation to a clear sky before the cloud appeared. A similar diagnosis would, no doubt, dispel many illusions in regard to records of exceptional temperature depressions produced by nocturnal radiation.

The area of sky included within the instrumental aperture was about 24 square degrees, or a circle ten times the diameter of the moon. The heat-measuring instrument was standardized as follows:

(1) For a temperature 33° F. below that of the instrument, the radiation to a tin plate screen in a distant black shelter at the temperature of the outside air (tin plate reflecting to the black walls of the shelter or to the ground at air temperature) gave an average galvanometer deflection of −0·64 div. per degree Fahrenheit in fair weather, and −0·61 in foggy weather.

(2) Black card at outside air temperature, suspended outside the aperture in the north wall of the observatory and exposed as in all other cases by withdrawing a screen of tinned wood within the building, having both the inside temperature and very feeble radiating power, gave for an external temperature 24° below that of the instrument, −0·65 div. per degree F.

(3) Snow at an average temperature 44° below that of the instrument gave −0·65 div. per degree F.

(4) A black radiator (boiling and near at hand) having the cavernous shape appropriate to an ideal radiator, and compared with a screen at air temperature, gave for an excess of +192° F.

a deflection of +0·60 div. per degree F. The smaller deflection per degree of excess in this case is caused by the smaller transmission of radiation from the hotter body whose maximum of energy in the spectrum comes within the limits of the great Ξ band of aqueous vapor, while the radiation from bodies at temperatures below the freezing point has its maximum in the spectral energy-curve at a greater wave-length, and, consequently, is less absorbed by the aqueous vapor of the atmosphere. Herein lies the explanation of the approximate fulfillment of Newton's law of radiation within the range of temperature included in these observations. In consequence of these variations in the composition of the radiations to be compared, the observations of these distant radiators at low temperatures may be represented by a rectilinear proportionality of 0·65 div. per degree F., neglecting the curvature which would affect the representation of a radiation at higher temperature or with greater absorption.

WINTER MEASUREMENTS.

Date.	Time.	STATE OF THE SKY.	External air temperature	Relative humidity.	Temperature of instrument.	Galvanometer deflection.	Effective temperature of Sky.	
1909							F.	C.
			°		°		°	°
Jan. 20	4 p.	Fahrenheit temperature=	37·8	0·68	64	----	----	----
	5:38 p.	Zenithal sky (milky blue)	---	---	65	−39·0	+ 4·9	−15·1
	8:37 p.	Overcast (deflection varying from −24·4 to −38·6 as cloud became thinner and stars faintly visible)	---	---	66	−28·6	+22·0	− 5·6
Jan. 21	8:08 a.	Zenithal sky (deflection changing from −40·0 to −34·1 as blue sky turned to thinnest cirro-stratus)	24	---	61	−36·1	+ 5·5	−14·7
	8:35 a.	Thin cirro-stratus	26	--	62	−23·6	+25·7	− 3·5
	9:10 a.	Cirro-stratus visibly thinner	---	---	63	−35·7	+ 8·1	−13·3
	11:41 a.	Good blue sky (milky blue)	41	0·79	66	−36·9	+ 9·2	−12·7
	12:35 p.	“ “ “	42	---	66	−37·9	+ 7·7	−13·5
	4:12 p.	Faint filo-cirrus, slight mist	43	---	66	−34·8	+12·5	−10·8
	5:45 p.	“ “ (?) Too dark for cloud observations. Probably high cirrus	---	---	66	−34·5	+12·9	−10·6
Jan. 29	10:55 a.	Zenithal sky deep blue. A few cirri	30	---	56	−43·1	−10·3	−23·5
	11:50 a.	Feathery flocculent cirrus and cirro-stratus	31	0·78	56	−37·7	− 2·0	−18·9
Feb. 1	11:03 a.	Zenithal sky deep blue. Quite clear	8	---	53	−71·0	−56·2	−61·5
	10:40 p.	“ “ clear	---	---	59	−47·0	−13·3	−25·2
	11:12 p.	Thin cirro-stratus. Lunar halo	---	---	59	−30·8	+11·6	−11·3
	11:25 p.	“ “ “ “	9·5	0·40	59	−28·5	+15·2	− 9·3
Feb. 2	10:27 a.	Zenithal sky milky blue	19	0·77	57	−34·0	+ 4·7	−15·2
Feb. 3	9:21 a.	Zenithal sky a good blue	10	0·86	60	−53·5	−22·3	−30·2
	12:39 p.	Exceedingly faint cir-str. (scarcely more than a suspicion)	16	---	61	−39·8	− 0·2	−17·9
	5:10 p.	Apparently clear	20	0·76	61	−39·9	− 0·4	−18·0
	7:38 p.	Zenithal sky quite clear	---	---	61	−49·5	−15·2	−26·2
	8:30 p.	“ “	12	0·65	61	−47·9	−12·7	−24·8

SUMMER MEASUREMENTS.

Date.	Time.	STATE OF THE SKY.	External air temperature.	Relative humidity.	Dew-point.	Temperature of instrument.	Galvanometer deflection.	Depression of temperature.	Effective temperature of Sky.	
1909									F.	C.
							div.	°	°	°
July 3	5:10 p.	Zenithal sky a good blue ------	F.	---	F.	72°	−34·9	−53·7	+18·3	− 7·6
	5:20 p.	(A few widely scattered cumuli)	---	---	---	72	−33·9	−52·2	+19·8	− 6·8
	5:48 p.	------------------------------	---	---	---	72	−30·7	−47·2	+24·8	− 4·0
	5:55 p.	------------------------------	---	---	---	72	−32·5	−50·0	+22·0	− 5·6
	7:05 p.	------------------------------	58°	---	---	72	−39·5	−60·8	+11·2	−11·6
	9:20 p.	------------------------------	57	0·77	50	72	−32·9	−50·6	+21·4	− 5·9
		Mean sky temperature for the day= ----------------------	---	---	---	---	-----	-----	-----	° − 6·9
July 4	7:50 a.	Deep blue sky ----------------	---	---	---	74	−29·8	−45·8	+28·2	− 2·1
	8:00 a.	(A few white fracto-cumuli) ---	---	---	---	74	−28·7	−44·2	+29·8	− 1·2
	8:20 a.	------------------------------	67	0·72	57·5	74	−35·7	−54·9	+19·1	− 7·2
	3:53 p.	------------------------------	72·4	0·69	62	78	−27·5	−42·3	+34·7	+ 1·5
	5:29 p.	(After a shower) --------------	---	---	---	72	−29 5	−45·4	+26·6	− 3·0
		Mean sky temperature for the day= ----------------------	---	---	---	---	-----	-----	-----	° − 2·4
July 5		Deep blue sky. Quite clear ---	---	---	---	---	-----	-----	-----	-----
		MEASURES AT VARIOUS ALTITUDES								
	7:30 a.	Sky at zenith ------------------	66·7	0·72	57	72	−29·1	−44·8	+27·2	− 2·7
	9:00 a.	Sky 5° above east horizon -----	---	---	---	78	−12·2	−18·8	+59·2	+15·1
	9:15 a.	" " " -----	---	---	---	79	−10·8	−16·6	+62·4	+16·9
	9:45 a.	Sky 15° above east horizon ----	---	---	---	80	−18·8	−28·9	+51·1	+10·6
	10:10 a.	" " " ----	---	---	---	80	−23·6	−36·3	+43·7	+ 6·5
	10:45 a.	Sky 30° above east horizon ----	---	---	---	80	−22·3	−34·3	+45·7	+ 7·6
	10:55 a.	" " " ----	---	---	---	80	−20·9	−32·2	+47·8	+ 8·8
	11:55 a.	Sky at zenith—deep blue -------	75	0·62	61	80	−28·0	−43·1	+36·9	+ 2·7

The meteorological conditions on the morning of February 4th, 1909, have already been described. Owing to the high relative humidity, radiation of long wave-length was much obstructed and the observations of sky radiation are not comparable with those of other dates. They are as follows:

div.
5 : 15 *a*, air 0°, instrument 60°, sky deflection ---------- = − 53·1
5 : 35 *a*, deflection from snow at − 6° F. ------------ = − 42·1
10 : 33 *a*, (relative humidity = 0·925) deflection from snow at + 20° F. -------------------------- = − 20·7
10 : 48 *a*, deflection from sky ----------------------- = − 37·1

The sky, which at first was a uniform cirro-stratus with strong halo, had changed at the last observation to banded cirro-stratus and cirro-cumuli. Halo fainter. The effective temperature of the sky was

at 5 : 15 *a*, — 53·1/·65 = 81·7° F. lower than the instrument, or .... — 22°F.
at 10 : 48 *a*, — 37·1/·65 = 57·1 lower than the instrument, or .... — 3° F.

Here, with little change in the amount of cloud, the sky deflection was persistently that of a surface whose effective temperature was some 20° F. colder than the air. A progressive air movement from the south was going on, and the sky deflection registers the increase in the temperature of the cloud layer.

No attempt was made to pick out the times of best sky (except for the altitude measures), but the observations were taken at irregular intervals when it happened to be convenient to secure them. Each recorded galvanometer deflection is the mean of five successive readings which were quite consistent except in the cases noted of rapidly changing sky.

I will now compare a few of the best of these readings with some made many years ago at Allegheny Observatory, in which only the clearest nights, suitable for refined lunar measures of radiation, were used. The altitude of the Westwood Observatory is some 200 feet above sea-level, and that of the (old) Allegheny Observatory is 1145 feet. Temperatures are Centigrade.

Allegheny, Pa.			Westwood, Mass.					
Winter			Winter			Summer		
Sky temperature	Air temperature	Dew-point	Sky temperature	Air temperature	Dew-point	Sky temperature	Air temperature	Dew-point
—54°	— 1·5°	— 7·7°	—61·5°	—13·3°	—22·2°	—6·9°	+13·9°	+10·0°
—67	—12·4	—22·6	—30·2	—12·2	—13·9	—2·4	+19·4	+14·2
—44	— 9·2	—14·9	—24·8	—15·8	—16·1	0·0	+21.6	+15·0

On the whole, the effective temperature of the sky is lower when the dew-point is lower and the aqueous obstruction of radiation to space is least; but it will be noticed that the observed effective temperature has never been found lower than that of the isothermal layer whose behavior in this respect is similar to that of a dense cloud which reflects back all surface radiation of a particular sort; or the isothermal layer is like a black solid of absolute temperature approximately $T=218^\circ$ Abs. C., λ max.$=13{\cdot}5\mu$, which is opaque to radiation similar to its own, but transmits a portion of the radiation of shorter wave-length from a solid body at $T=289^\circ$, and λ max.$=10{\cdot}2\ \mu$.

Taking a single day of clear sky (February 3d), the day sky at 9 : 21 A. M. was 7° F. colder than the night sky at 8 : 30 P. M., conditions of air temperature and humidity being not very different. The change of apparent sky temperature from −22° F. at 9 : 21 A. M. to 0° F. near noon is about like that of the diurnal change of air temperature from +0·8° F. at 7 : 37 A. M. to +20·2° F. at 4 P. M. The sky variation also follows the changing air temperature into the evening hours :

9 : 21 A. M.	Air	+10° F.	Sky	−22° F.	Difference	=	−32°
12 : 39 P. M.		+16		0			−16
8 : 30 P. M.		+12		−15			−27

Thus the noon sky on a clear day appears warmer, that is, less transmissive of telluric radiation, than the morning or evening sky. The noon air, as we know, is also less transmissive of solar radiation.

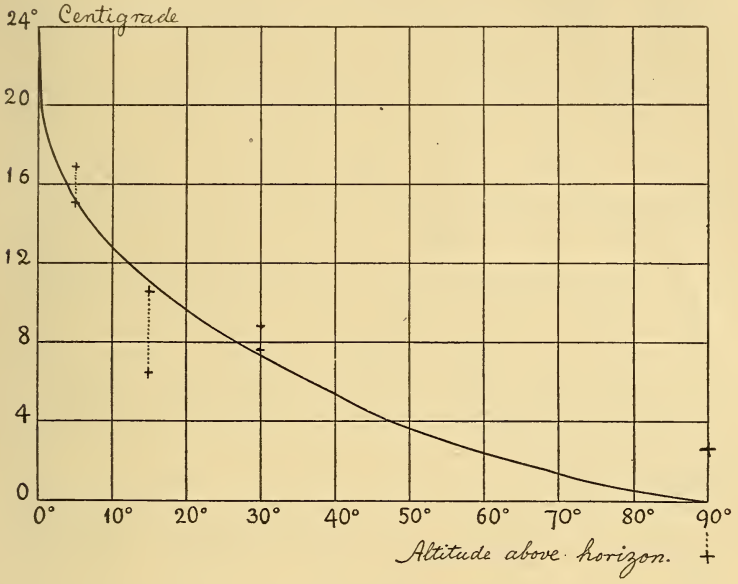
When, however, we average a considerable number of daylight observations of apparent sky temperature, including skies which are more or less contaminated with cirrus, and compare with similar night observations, there is not much difference. Thus ten night readings gave an average galvanometer deflection of −39·7 div. and twelve daylight observations gave a mean of —38·8 div., which are nearly identical. The temperature of the instrument varied only a few degrees from 60° F.

Finally, we may classify the observations according to the clearness of the sky as follows :

Very clear	Clear	Milky blue	Cirro-stratus	
−61·5° C.	−23·5° C.	−15·1° C.	−14·7° C.	—18·9° C.
−30·2	−25·2	−12·7	— 3·5	—11·3
−26·2	−18·0	−13·5	−13·3	— 9·3
−24·8	......	−15·2	−10·8	......
......	......	−17·9	−10·6	......
Mean −35·7° C.	−22·2° C.	−14·9° C.	......	—11·5° C.

The curve of apparent sky temperature and altitude above the horizon for July 5th is plotted in fig. 2. The curve is rather flat-topped. There is a slow change from the zenith to an altitude of 30°, but below 20° altitude the negative radiation to the sky diminishes rapidly, and at 5° altitude it sometimes hardly differs from the radiation to the ground.

FIG. 2.



Final Conclusions.

As an example of an average sounding-balloon ascent to the lower limit of the isothermal layer at latitude 52° and in the tropics we may take

	Air density at the surface	= 1·26 kgm / cu. m.	= 1 atm.
(Lat. 52°)	" " " 12000$^{\text{m}}$	= 0·3928 "	= 0·312 "
(Tropics)	" " " 15000$^{\text{m}}$	= 0·2810 "	= 0·223 "

That is to say, about one-fourth of the atmosphere is included in the isothermal layer, or there are 2000 cubic meters = 2586 kgm. of standard air over each square meter of surface at the isothermal limit. The specific heat of air being 0·239, if 35 large calories are received from the sun's rays at the outer surface on each square meter each minute, then (2856 × 0·239) / 35 = 19·5 minutes will be required for a rise of 1° C., if all the energy is absorbed; or if no more than 7 per cent of absorption occurs (an amount which might be inferred from the lowest estimates of the absorption bands in the solar spectrum), 19·5 / 0·07 = 279 minutes = 4·65 hours will be required for a rise of temperature of 1° C. in the entire mass, and the average diurnal fluctuation of temperature should not exceed 3° C., subject to what variation may arise from unequal distribution of absorbent substances. The large amount of heat required to maintain this great mass of air at a temperature of over 200° Abs. C., or to change its temperature by even a few degrees, must tend to keep the thermal condition constant, but the absence of a seasonal variation can only mean that the air is still impervious to the greater part of the radiation from a body of air at this temperature. The freer atmospheric radiation, of which there is also evidence upon entering this region, probably appertains to the radiant bands of shorter wavelength emitted by the aqueous vapor and other atmospheric constituents. These bands of shorter wave-length (for example, those constituting great Ξ) can not be very strongly emitted at this low temperature, but they serve to limit the rise of temperature attainable by absorption of solar radiation to a very narrow range, for if the temperature were to increase to only a small extent, the radiant power of aqueous vapor in these bands would grow at a much more rapid rate, because the temperature in question is nearly the critical one of greatest sensitiveness and most rapid percentage increase for these particular bands.

Each emission band of a discontinuous emission spectrum has some low temperature at which it begins to appear, succeeded after a certain amount of development by a critical period of most rapid change as the temperature continues to rise, and finally reaching a steady stage of maximum development, when there is little further change of relative intensity, but thereafter, each component homogeneous ray in narrowly limited bundles within the band increases according to some power of the absolute temperature not far from the fourth or fifth through a considerable range, and matches the corresponding radiation of a full radiator within these narrow limits.

NOTE.—When developed to their greatest extent, the maxima of emission in line or band spectra are found to agree with the radiation for corresponding wave-lengths in the spectrum of a black body. The statement in the text is only an approximation. The variation of homogeneous radiations can not be expressed as simply as this except close to the spectral maximum.

Approximate rates of increase of homogeneous radiations with increasing temperature were first obtained throughout the infra-red spectrum at Allegheny Observatory in 1885 by means of the spectro-bolometer, and the fact that the maximum ordinate of a spectral energy-curve moves towards the shorter wave-lengths with increasing temperature was discovered at the same time. The experiments were described by Langley in Annales de

Chimie et de Physique (6) ix, pp. 433–506, 1886, where, however, the wave-lengths and temperatures are very imperfectly estimated. The same remark applies to the "Curve Showing Movement of the Maximum," published in the memoir on "The Temperature of the Moon," by S. P. Langley, assisted by F. W. Very (National Acad. Sci., vol. iv, part 2, plate ix, Washington, 1889), but does not so much affect the curves showing "Rates of Emission for Different Deviations" (op. cit. plate 5) in which the temperature-excesses are limited to fairly trustworthy values, less than 200° C. The ordinates (emission of approximately homogeneous radiations corresponding to given rock-salt deviations) suffer somewhat from defect, because the bolometer was not a complete absorbent. This instrumental deficiency was subsequently remedied by Paschen, who devised what may be called a "repeating" bolometer, or thermopile, where the heat-measuring instrument is at the center of a hemispherical mirror, pierced by an aperture for admitting the radiation, and where those rays which are not immediately absorbed and converted into heat are diffusely reflected to the mirror and come back again for one or more subsequent absorptions at the sensitive surface, until the last vestige of radiant energy has been utilized.

The Allegheny measures were revised by me in 1896 and given with correctly assigned wave-lengths, and on the normal scale, in a paper, "Further Considerations in regard to Laws of Radiation" (Astrophysical Journal, vol. iv, p. 38, June, 1896), but still with the same temperatures which had been originally assigned from known melting points. These temperatures, or at least the higher ones, were largely overestimated, because no allowance was made for the fact that the outermost layer of a plane, vertical, radiating surface, of large temperature excess, is cooled so rapidly by aerial convection, that even a highly conductive metal (heated from the back side) develops a very steep subsurface temperature-gradient, and all ordinary methods of measuring the real temperature of the radiating surface fail. Paschen first determined the true temperatures by using a radiator of cavernous shape, employing a "repeating" principle in the radiator, as well as in the heat-measuring instrument. This principle had been known in the theory for some time, and was reasoned out mathematically by Ferrel ("Recent Advances in Meteorology," p. 97, Washington, 1886), but was first practically applied in these researches by Paschen, from which Wien's law was confirmed in a very satisfactory way.

The emission of homogeneous rays may be expressed by the equation

$$J = C_\lambda T^\chi$$

where $\chi = 4$ to 5 for wave-lengths (λ) not far from the maximum in the spectral energy-curve of the black body at absolute temperature T, and C_λ is an emission constant, varying with λ, and to a still greater extent with the nature of the emitting substance and the thickness of its emitting layer. At much higher temperatures, for which the spectral maximum has passed to wave-lengths shorter than λ, the emission of wave-length λ requires a smaller value of χ; and for low temperatures where rays of wave-length λ are first beginning to be emitted, the rate of increase of the incipient radiation is much more rapid, so that χ assumes large values. To show this, I will take from the Allegheny curves of plate 5 (op. cit.) ratios of the homogeneous radiation of lampblack at three temperature-excesses:

$$\begin{aligned}\theta_a &= 60^\circ = T_2 - T_1 = 326^\circ - 266^\circ \text{ abs. C.}\\ \theta_b &= 120 = 386 - 266\\ \theta_c &= 180 = 446 - 266\end{aligned}$$

This eliminates any imperfection in the absorbent process, since the errors are the same in the components of each series, though varying from one series to the next. Radiation of wave-length 1μ is incipient for such excesses as these, and the exponent of T reaches 10, but falls below 4 for the longest waves.

	a	*b*	*c*
λ 11·3 μ (R. S. deviation = 36°)	1	2·7	4·7
$T_2^4 - T_1^4$	1	2·7	5·5
λ 9·60 μ (R. S. deviation = 37°)	1	3·2	6·3
λ 7·42 μ (" " = 38°)	1	2·9	6·4
$T_2^5 - T_1^5$	1	3·1	6·9
λ 4·28 μ (R. S. deviation = 39°)	1	4·2	11·2
$T_2^7 - T_1^7$	1	4·0	11·5
λ 0·98 μ (R. S. deviation = 40°)	1	8·7	22·7
$T_2^{10} - T_1^{10}$	1	6·1	26·2

The same thing may be shown from results at somewhat higher temperatures obtained by Paschen (Astrophysical Journal, vol. x, p. 52, June, 1899), from which I take radiation ratios for the temperature-excesses:

$\theta_a = 89·4° = T_2 - T_1 = 462·4° - 373·0°$ abs. C.
$\theta_b = 204·1 = 577·1 - 373·0$
$\theta_c = 350·0 = 723·0 - 373·0$

	a	*b*	*c*
λ 7·783 μ	1	2·25	4·38
$T_2^2 - T_1^2$	1	2·60	5·13
λ 6·263 μ	1	2·73	6·18
$T_2^4 - T_1^4$	1	3·48	9·63
λ 4·663 μ	1	3·76	11·14
$T_2^6 - T_1^6$	1	4·84	19·79
λ 3·355 μ	1	6·32	27·99
$T_2^7 - T_1^7$	1	5·78	29·07

If we compute homogeneous radiations by Wien's law for T = 5000°, 6000°, 7000° abs. C., the ratios in the next table are obtained:

	a	*b*	*c*
$T_2^3 - T_1^3$	1	1·73	2·74
$\lambda = 1·0\ \mu$	1	1·72	2·42
$\lambda = 0·8\ \mu$	1	1·80	2·76
$T_2^4 - T_1^4$	1	2·07	3·84
$\lambda = 0·6\ \mu$	1	2·26	4·00
$T_2^5 - T_1^5$	1	2·49	5·38
$\lambda = 0·5\ \mu$	1	2·62	5·17
$T_2^6 - T_1^6$	1	2·99	7·53
$\lambda = 0·4\ \mu$	1	3·36	8·05

If we draw the curve of absolute temperature from the highest point of observation up to an altitude of 80 km. and compare it with the extension of the observed curve from 0 to 10 km., also continued to 80 km. as in fig. 1, the included area above 10 km. has been nearly doubled (2·11 : 1·00), or the heat stored in the isothermal layer has been increased to some such extent by the protective mechanism of the atmosphere.

Altitude (km.)	0	5	10	15	20	25	30	35	40
T (isothermal)	266	241	206	198	203	212	212	210	200
T (by regular fall)	266	241	206	179	150	125	100	78	55
Difference	0	0	0	19	53	87	112	132	145

Altitude (km.)	45	50	55	60	65	70	75	80
T (isothermal)	186	143	120	92	52	35	20	10
T (by regular fall).	40	30	22	16	12	8	5	3
Difference	146	113	98	76	40	27	15	7

Comparing the two curves, we see that at an altitude of 40 km. the temperature is probably about 150° C. higher than it would be were it not for the heat derived from the absorption of solar radiation.

Although the air transmits a variable but considerable fraction of telluric radiation to outer space and thus possesses selective absorption, it is a curious fact that for an ultimate remnant of this radiation, the atmosphere behaves as if it were an impervious or perfectly reflecting solid for all wave-lengths emitted by a body at about −60° or −70° C. The greatest cold observed in the Arctic regions in winter seldom falls below the latter temperature. This, therefore, is the effective temperature of that atmospheric layer which limits the output of terrestrial radiation. The action would be the same if the air layer were a perfectly absorbent one and at the given temperature, or if the phenomenon were one of reflection and the reflecting layer at any temperature whatever within a wide range. For my present purpose it is not necessary to discriminate between these two cases.

The outcome of the process is that in temperate latitudes with the clearest skies there is a seasonal change in sky radiation determined by the presence or absence of aqueous vapor. Just as the abundance of aqueous vapor in the lower air in summer enables this substance to play the part of a conservator of surface heat, so there must be a similar conservator for the heat of the upper air, the heat in either case being derived from the sun's rays. The water vapor limits surface radiation mainly by the absorption in the great Ξ band situated on the short-wave side of the terrestrial radiant maximum which in sunshine lies between 9μ and 10μ. The great Δ band of carbon dioxide at $14{\cdot}7\mu$ occupies a somewhat similar position in respect to the maximum radiation of the upper air, but since this gas is too dense to reach the greatest heights, its action must be confined to the lower part of the layer, and if the upper air behaves like an opaque solid, its absorption spectrum beyond Δ must be a continuous succession of broad and intense bands. Water vapor has a number of bands in this part of the spectrum, but it does not seem probable that an atmospheric feature so seasonally constant as the isothermal region should be dependent on such a seasonally variable thing as atmospheric aqueous vapor, and we may rather anticipate that the conservation will be found to lie in some of the permanent gases, which here exchange rôles with the aqueous vapor of the lower air. In fact if we try to apportion the three factors of atmospheric temperature—absorbent, conservator, radiant—we shall find that the solid earth is the absorbent from which the lower air derives its heat by transference, the aqueous vapor is the conservator, being highly opaque to its own radiation and therefore compelling the lower air to radiate slowly by its poorest radiators, the air molecules. The latter constitute the *radiant* for the lower moist air.

In the isothermal region, aqueous vapor is the chief absorbent by reason of its numerous bands in the visible infra-red spectrum. Oxygen and carbon dioxide help a little, and ozone may contribute something towards the retention of the shortest solar ultra-violet waves. If the suggestions in the preceding paragraph are correct, carbon dioxide and some of the permanent gases are the chief conservators here, and the radiant is aqueous vapor through its emission bands between Ξ and Δ, and to some extent through Ξ (although this emission is rather feeble at this lower temperature) together with ozone in the region from $9{\cdot}2\mu$ to $10{\cdot}0\mu$. Beyond great Δ, emission ceases, except that near the extreme outer limits of the layer the opaque gases become sufficiently attenuated to again act as radiators, when the temperature rapidly falls to absolute zero.

The most important fact derived from this research is that apparently the effective temperature of the sky never descends below the temperature of the isothermal layer even in the coldest and driest weather and with the purest skies. This fact favors the supposition that this layer is almost completely absorbent for radiation beyond about 14μ, that the effect is one of emission rather than of almost total reflection, and that the apparent effective temperature of the sky is the actual temperature of the upper air and its clouds, reaching, when the sky is clear and the lower air sufficiently transmissive, the temperature of the isothermal layer itself.

Westwood Astrophysical Observatory,
Westwood, Massachusetts.
August 22, 1912.

ART. XXXIV.—*On the Deviation Produced by Prisms*; by H. S. UHLER.

BY consulting all available standard reference books and scientific journals, the writer has been unable to find a discussion of the general case of refraction of oblique rays by a single prism which will enable the reader to form a clear or adequate conception of the dependence of the total deviation upon the angles defining the direction of the incident ray. The reference books give but little more than a formula connecting the deviation (D) of the oblique ray with the deviation (E) of the projection of the ray on a principal section of the prism, and with the angle (η_1) which the incident ray makes with such a section. Furthermore, the formulæ to be found in the books are not equivalent, most authors write

$$\cos \tfrac{1}{2}D = \cos \tfrac{1}{2}E \cos \eta_1,\text{*}$$

(apparently following Heath), and one author, at least, writes

$$\sin \tfrac{1}{2}D = \sin \tfrac{1}{2}E \cos \eta_1.\dagger$$

Neither equation throws much light on the subject because E is a function of η_1 and of another angle, so that D is an implicit function of two independent variables. On the other hand, the journal articles treat, in a fragmentary manner, of certain special problems connected with the general case of the deviation of oblique rays, consequently it requires a disproportionate amount of time to find out what has already been done. Unfortunately not all of these articles are trustworthy. Since this state of affairs exists, and since the question is not without interest to students of geometrical optics, it seems desirable to collect in one place the correct results hitherto obtained, to supplement these results by original investigation, when necessary, and to present in graphical form all the facts amenable to such treatment. In other words, the endeavor will be made in the present paper to treat the problem of prismatic deviation in as complete and thorough a manner as possible.

The entire discussion will have reference to the case of a single prism with unlimited plane faces, and surrounded by one medium whose absolute index of refraction is less than the

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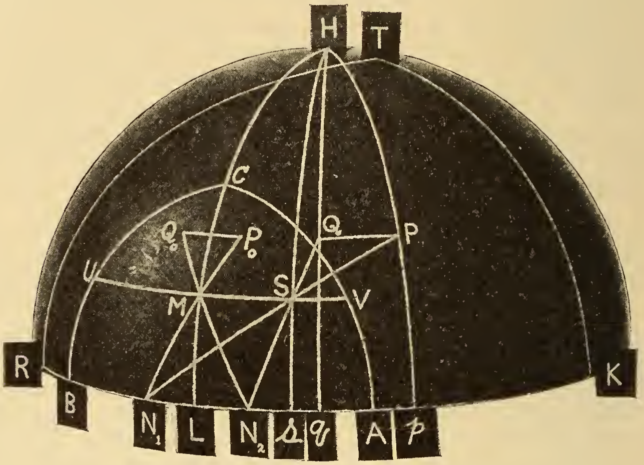
* S. Czapski: Winkelmann's "Handbuch der Physik," vol. vi, p. 189, 1906; R. S. Heath: "Geometrical Optics," p. 32, 1887; H. Konen: Kayser's "Handbuch der Spectroscopie," vol. i, p. 262, 1900; F. Löwe: M. von Rohr's "Die Theorie der optischen Instrumente," vol. i, p. 428, 1904; J. P. C. Southall: "The Principles and Methods of Geometrical Optics," p. 126, 1910.

† J. Walker: "The Analytical Theory of Light," p. 12, 1904.

absolute index of the material of the prism. The relative index of the prism will be denoted by n. For the sake of uniformity, the definitions of the quantities involved will be the same as given in Southall's "Geometrical Optics." Also, with few exceptions, the notation of this author will be followed.

In order to fix the ideas and to make the definitions of the symbols used in the following pages as clear as possible, great-circle and other arcs were drawn to scale on a hemispherical blackboard, the points of intersection were lettered, and the whole was then photographed. In figure 1, which is a reproduction of this photograph, let the center of the sphere be denoted by O. The great-circle N_1N_2 corresponds to a principal plane of the prism. One pole of this circle is shown at H. The normals to the incidence and emergence faces are represented by ON_1 and ON_2, in the order named. With N_1 and N_2 as centers let arcs of small-circles, AC and BC, be described having such spherical radii as to subtend at the center of the sphere angles equal to the critical angle, $c = \sin^{-1}\frac{1}{n}$. [Only half of each arc is shown in the figure. The points homologous to C and H will be denoted by C′ and H′.] These small-circles must intersect if transmission is to be possible. The extremity (S) of the ray inside the prism must not lie outside of the smaller region bounded by the two small-circle arcs, since total reflection is to be excluded.

Fig. 1.



$\angle N_1ON_2 = \beta =$ angle of prism,
$\angle N_1OP = \alpha_1 =$ " " incidence, 1st face,
$\angle N_1OS = \alpha_1' =$ " " refraction, " "
$\angle N_2OS = \alpha_2 =$ " " incidence, 2d "
$\angle N_2OQ = \alpha_2' =$ " " emergence, " "
$\angle QOP = D =$ deviation of oblique ray,
$\angle qOp = E =$ " " projected ray,

$$\left.\begin{array}{ll}\angle pOP & = \eta_1, \\ \angle sOS & = \eta_1', \\ \angle qOQ & = \eta_2',\end{array}\right\} = \text{altitudes,}$$

$$\left.\begin{array}{ll}\angle N_1Op & = \gamma_1, \\ \angle N_1Os & = \gamma_1', \\ \angle N_2Os & = \gamma_2, \\ \angle N_2Oq & = \gamma_2'\end{array}\right\} = \text{azimuths.}$$

Angles will be counted positive when generated by a right-handed rotation about the axis $\overrightarrow{OH}$. Also, the only angles in the above list which may exceed $\frac{1}{2}\pi$ and still correspond to physical reality are β, D and E. [For further details of fig. 1, see p. 407.]

$$\beta = \gamma_1' - \gamma_2 \tag{1}$$

$$E = \gamma_1 - \gamma_2' - \beta \tag{2}$$

Since the prism is surrounded by the same medium

$$\eta_2' = \eta_1.$$

This fact was noted by Bravais as early as 1845. He says:* "... ce qui nous donne cette *première loi de la réfraction oblique dans les prismes* 'Le rayon émergent et le rayon immergent sont également inclinés sur le plan de la section principale.'" Consequently the triangle QPH is isosceles, and hence

$$\sin \tfrac{1}{2}D = \sin \tfrac{1}{2}E \cos \eta_1 \tag{3}$$

This relation was used by Bravais for the case of minimum deviation. He gave

$$\text{“}\sin \tfrac{1}{2}\Delta = \sin \tfrac{1}{2}D \cos H\text{”}$$

on page 83, *loc. cit.* Since, in general, $\cos \eta_1 < 1$ relation (3) shows that

$$D < E.$$

In spite of this obvious inequality, several modern authors write, with Heath,

$$\cos \tfrac{1}{2}D = \cos \tfrac{1}{2}E \cos \eta_1.$$

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* A. Bravais: Journal de l'Éc. Polytechn. 18, 30^{e} Cahier, p. 79, 1845.

[See prefatory remarks.] Apparently, the only other fact which flows directly from (3) alone is this: if η_1 is kept constant while the azimuths are allowed to vary, D and E will decrease or increase together, so that if either passes through a stationary value so also will the other pass through the same kind of critical value simultaneously.

In addition to the relations given above, the following equations will be found useful:

$$\sin \eta_1 = n \sin \eta_1' \tag{4}$$

$$\sin \gamma_1 = \nu \sin \gamma_1' \tag{5}$$

$$\sin \gamma_2' = \nu \sin \gamma_2 \tag{6}$$

where $\nu = n \cos \eta_1' \sec \eta_1 = \sqrt{n^2 + (n^2 - 1) \tan^2 \eta_1}$.

Since, as will be shown later, the general deviation may be expressed as an explicit function either of γ_1' and η_1' or of γ_1 and η_1 (c or n and β being supposed given), two methods, at least, for exhibiting all possible variations of D suggest themselves. One plan would be to construct a surface outside of the sphere of figure 1 which would be the locus of the extremity of the extension either of the radius OS or of OP, the length of the extended segment to be taken proportional to the value of the deviation at the points S or P respectively. This process would be analogous to the scheme often used for showing the distribution of static electricity over the surface of an insulated conductor. For various reasons the model with extended radii would be inconvenient for publication. The other method is to construct a surface with rectangular coördinates, considering D as dependent variable, (axis of z), with γ_1' and η_1' or with γ_1 and η_1 as independent variables, (axes of x and y). In the following pages the properties of the surfaces referred to rectangular frames will be discussed, and diagrams of certain plane sections of these surfaces will be given.

Instead of deriving an explicit function of D in terms of γ_1' and η_1' it will be found preferable to replace the coördinate γ_1' by λ, where $\lambda = \gamma_1' - \frac{1}{2}\beta$. Furthermore, all square-root operators will be understood as meaning only the positive root. From (2)

$$\cos E = \cos\beta \sin\gamma_1 \sin\gamma_2' + \sin\beta \sin\gamma_1 \cos\gamma_2' - \sin\beta \cos\gamma_1 \sin\gamma_2' + \cos\beta \cos\gamma_1 \cos\gamma_2'.$$

From (5)

$$\sin\gamma_1 = \nu \sin(\lambda + \tfrac{1}{2}\beta)\,;$$

from (1) and (6)

$$\sin\gamma_2' = \nu \sin(\lambda - \tfrac{1}{2}\beta)$$

therefore, since $\gamma_1 \ngtr \frac{1}{2}\pi$ and $\gamma_2' \ngtr \frac{1}{2}\pi$,

$$\left.\begin{aligned}\cos E = {} & \nu^2 \cos\beta \sin(\lambda + \tfrac{1}{2}\beta) \sin(\lambda - \tfrac{1}{2}\beta) \\ & + \nu \sin\beta \sin(\lambda + \tfrac{1}{2}\beta)\sqrt{1 - \nu^2 \sin^2(\lambda - \tfrac{1}{2}\beta)} \\ & - \nu \sin\beta \sin(\lambda - \tfrac{1}{2}\beta)\sqrt{1 - \nu^2 \sin^2(\lambda + \tfrac{1}{2}\beta)} \\ & + \cos\beta\sqrt{[1 - \nu^2 \sin^2(\lambda + \tfrac{1}{2}\beta)][1 - \nu^2 \sin^2(\lambda - \tfrac{1}{2}\beta)]}\end{aligned}\right\} \quad (7)$$

From (3) and (4)

$$\sin^2 c \cos D = \sin^2 \eta_1' + (\sin^2 c - \sin^2 \eta_1') \cos E,$$

hence

$$\left.\begin{aligned}&\sin^2 c \cos D = \sin^2 \eta_1' + \cos\beta \sin(\lambda + \tfrac{1}{2}\beta) \sin(\lambda - \tfrac{1}{2}\beta) \cos^2\eta_1' \\ & + \sin\beta \sin(\lambda + \tfrac{1}{2}\beta) \cos\eta_1' \sqrt{\cos^2(\lambda - \tfrac{1}{2}\beta) \cos^2\eta_1' - \cos^2 c} \\ & - \sin\beta \sin(\lambda - \tfrac{1}{2}\beta) \cos\eta_1' \sqrt{\cos^2(\lambda + \tfrac{1}{2}\beta) \cos^2\eta_1' - \cos^2 c} \\ & + \cos\beta\sqrt{[\cos^2(\lambda - \tfrac{1}{2}\beta) \cos^2\eta_1' - \cos^2 c][\cos^2(\lambda + \tfrac{1}{2}\beta) \cos^2\eta_1' - \cos^2 c]}\end{aligned}\right\} \quad (8)$$

This is the equation of the $\lambda\eta_1'D$ surface, in the sense that all values of D which correspond to physical reality must satisfy relation (8). Inspection of (7) and (8) shows that, when η_1' is kept constant, E and D are symmetrical with respect to the locus $\lambda = 0$, *i. e.*, the great-circle H′LH of fig. 1. [This property may also be deduced by simple geometrical considerations.] This symmetry shows that E and D have stationary values for $\lambda = 0$. That these critical values are minima is an immediate consequence of the following premises: (*a*) the form of (7) does not alter when ν assumes different values, such as $\nu = n$ and $\nu > n$; (*b*) a prism of index n and angle β with a ray of obliquity η_1' is equivalent to a prism of greater effective index ν and angle β with a ray of zero altitude; (*c*) when $\lambda = 0$, $(\gamma_1' = -\gamma_2 = \frac{1}{2}\beta)$, the ray in a principal plane experiences minimum deviation, as is very well known. In fig. 1, Q_0P_0 represents the minimum of all deviations along the small-circle UV, whose altitude, LM, has any constant value. The greatest deviations corresponding to this altitude and having physical meaning pertain to the points U and V.

To find out how the minima of D vary with η_1', (along the arc H′LH), it is only necessary to put $\lambda = 0$ in equation (8) and to differentiate D_0 with respect to η_1', where D_0 denotes the value of D when $\lambda = 0$. Then

$$\frac{1}{\sin\eta_1'} \cdot \frac{dD_0}{d\eta_1'} = \frac{2 \sin\beta \sin\frac{1}{2}\beta(\cos\frac{1}{2}\beta \cos\eta_1' - \sqrt{\cos^2\frac{1}{2}\beta \cos^2\eta_1' - \cos^2 c}\ )^2}{\sin^2 c \sin D_0 \sqrt{\cos^2\frac{1}{2}\beta \cos^2\eta_1' - \cos^2 c}}$$

Consequently

$$\frac{1}{\sin \eta_1'} \cdot \frac{dD_0}{d\eta_1'}$$

is always positive, so that the minimum deviation increases with the obliquity of the ray. This includes the theorem that for symmetric passage in a principal plane the deviation is an absolute minimum. Since D_0 increases with η_1', or η_1, the equation

$$\sin \tfrac{1}{2}E_0 = \sin \tfrac{1}{2}D_0 \sec \eta_1$$

shows that E_0 increases with η_1. [The same conclusion follows at once from the usual relation $\sin \frac{1}{2}(E_0 + \beta) = \nu \sin \frac{1}{2}\beta$, since ν increases with η_1 and $\frac{1}{2}(E_0 + \beta)$ is acute.]

The first valid proof of the existence of the absolute minimum seems to have been given by Sir Joseph Larmor,[*] although the truth involved was generally recognized for a number of years before.[†] Nevertheless, Larmor's article has been overlooked by later writers because, apparently without exception, they have continued to give a fallacious demonstration based on the incorrect formula

$$\cos \tfrac{1}{2}D = \cos \tfrac{1}{2}E \cos \eta_1.$$

[See foot-note page 389.] In the year 1909 the present writer published a rigorous proof of the theorem of the absolute minimum.[‡] He desires to state that, at the time, he too was not aware of the existence of Larmor's article. However, the force of the later paper is not entirely lost because (*a*) the demonstration is altogether different from Larmor's, (*b*) its main object was to direct attention to the fallacy of the cosine relation, and (*c*) it gives a table of minimum deviations for the special case of $\beta = \frac{1}{3}\pi$ and $n = 1{\cdot}65$.

Keeping η_1' constant, as λ increases from zero, $\cos(\lambda + \frac{1}{2}\beta)\cos\eta_1' - \cos c$ decreases until it passes through zero and eventually becomes negative. In equation (8), the second and third radicals become imaginary when

$$\cos(\lambda + \tfrac{1}{2}\beta)\cos\eta_1' < \cos c,$$

hence the equation of the small-circle boundary C′AC, of the region of real D, may be written

$$\cos(\lambda + \tfrac{1}{2}\beta)\cos\eta_1' = \cos c \qquad (9)$$

In like manner, the equation of the small-circle C′BC is found to be

$$\cos(\lambda - \tfrac{1}{2}\beta)\cos\eta_1' = \cos c. \qquad (10)$$

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[*] J. Larmor: Proc. Camb. Phil. Soc., vol. ix, p. 109, 1896.

[†] R. S. Heath: A Treatise on Geometrical Optics, Cambridge, 1887, p. 32.

[‡] H. S. Uhler: This Journal, vol. xxvii, p. 223, 1909.

[Obviously, formulæ (9) and (10) may be obtained directly from the relations $\cos c = \cos\gamma_1' \cos\eta_1'$ and $\cos c = \cos\gamma_2 \cos\eta_1'$.] The equation of the $\lambda\eta_1'$ boundary locus may also be written

$$\sin\lambda = \pm[\cos\tfrac{1}{2}\beta\sqrt{\sin(c+\eta_1')\sin(c-\eta_1')} - \sin\tfrac{1}{2}\beta\cos c]\sec\eta_1', \tag{11}$$

the upper or lower sign to be taken according as points on C′AC or C′BC are desired respectively. When referred to the rectangular coördinate frame $\lambda\eta_1'D$, the four acute angles which these boundary loci make with the η_1'-axis are each numerically equal to

$$\tan^{-1}[\sec c\cot\tfrac{1}{2}\beta\sqrt{\sin(c+\tfrac{1}{2}\beta)\sin(c-\tfrac{1}{2}\beta)}] \tag{12}$$

On the other hand, the λ-axis is normal to the small-circle boundaries. The coördinates of the points A and B are respectively

$$\left.\begin{array}{lll} & \lambda = +(c-\tfrac{1}{2}\beta), & \eta_1' = 0, \\ \text{and} & \lambda = -(c-\tfrac{1}{2}\beta), & \eta_1' = 0. \end{array}\right\} \tag{13}$$

At C and C′,

$$\left.\begin{array}{ll} & \lambda = 0 \\ \text{and} & \eta_1' = \pm\cos^{-1}(\cos c\sec\tfrac{1}{2}\beta). \end{array}\right\} \tag{14}$$

For simultaneous grazing incidence and emergence, formula (8) reduces to

$$\sin\tfrac{1}{2}D = \cot c\sin\tfrac{1}{2}\beta. \tag{15}$$

For grazing incidence or grazing emergence in a principal plane equation (8) leads to

$$\sin\tfrac{1}{2}D = [\sqrt{\cos\tfrac{1}{2}\beta\cos(c-\tfrac{1}{2}\beta)} - \sqrt{\sin\tfrac{1}{2}\beta\sin(c-\tfrac{1}{2}\beta)}]\sqrt{\tfrac{1}{2}\csc c\sin\beta} \tag{16}$$

Equation (16) is equivalent to the following formulæ, which are suitable for logarithmic computation, namely

$$\left.\begin{array}{l} \cos(D+\beta) = \csc c\sin(c-\beta), \\ \sin\tfrac{1}{2}(D+\beta) = \sqrt{\csc c\sin\tfrac{1}{2}\beta\cos(c-\tfrac{1}{2}\beta)} \end{array}\right\} \tag{17}$$

Finally, for the absolute minimum of deviation, ϵ_0, (8) produces

$$\sin\tfrac{1}{2}\epsilon_0 = [\cos\tfrac{1}{2}\beta - \sqrt{\sin(c+\tfrac{1}{2}\beta)\sin(c-\tfrac{1}{2}\beta)}]\csc c\sin\tfrac{1}{2}\beta, \tag{18}$$

which is equivalent to the familiar formula

$$n = \frac{\sin\tfrac{1}{2}(\epsilon_0+\beta)}{\sin\tfrac{1}{2}\beta} \tag{19}$$

Of the various plane sections of the $\lambda\eta_1'D$ surface which may be imagined, the curves of constant deviation seem best adapted to showing the general contour of this surface. The next problem is, therefore, to derive a formula for λ in terms of β, ν, and E. Division of (6) by (5) gives

$$\csc\gamma_1'\sin\gamma_2 = \csc\gamma_1\sin\gamma_2',$$

hence

$$(\sin\gamma_2' \pm \sin\gamma_1)\csc\gamma_1 = (\sin\gamma_2 \pm \sin\gamma_1')\csc\gamma_1',$$

whence

$$\sin\tfrac{1}{2}(\gamma_2'+\gamma_1)\cos\tfrac{1}{2}(\gamma_2'-\gamma_1) = \nu\sin\tfrac{1}{2}(\gamma_2+\gamma_1')\cos\tfrac{1}{2}(\gamma_2-\gamma_1')$$

and

$$\cos\tfrac{1}{2}(\gamma_2'+\gamma_1)\sin\tfrac{1}{2}(\gamma_2'-\gamma_1) = \nu\cos\tfrac{1}{2}(\gamma_2+\gamma_1')\sin\tfrac{1}{2}(\gamma_2-\gamma_1').$$

Introducing relations (1) and (2) it results that

$$\sin\tfrac{1}{2}(\gamma_2'+\gamma_1) = \frac{\nu\cos\tfrac{1}{2}\beta\sin\lambda}{\cos\tfrac{1}{2}(E+\beta)}$$

and

$$\cos\tfrac{1}{2}(\gamma_2'+\gamma_1) = \frac{\nu\sin\tfrac{1}{2}\beta\cos\lambda}{\sin\tfrac{1}{2}(E+\beta)}$$

so that

$$\frac{\nu^2\cos^2\tfrac{1}{2}\beta}{\cos^2\tfrac{1}{2}(E+\beta)}\sin^2\lambda + \frac{\nu^2\sin^2\tfrac{1}{2}\beta}{\sin^2\tfrac{1}{2}(E+\beta)}\cos^2\lambda = 1 \qquad (20)$$

Consequently

$$\cos 2\lambda = \frac{\nu^2\left[\sin^2(\tfrac{1}{2}E+\beta)+\sin^2\tfrac{1}{2}E\right]-\sin^2(E+\beta)}{2\,\nu^2\sin\tfrac{1}{2}E\sin(\tfrac{1}{2}E+\beta)},$$

which is rational, or

$$\tan\lambda = \pm\cot\tfrac{1}{2}(E+\beta)\sqrt{\frac{\sin^2\tfrac{1}{2}(E+\beta)-\nu^2\sin^2\tfrac{1}{2}\beta}{\nu^2\cos^2\tfrac{1}{2}\beta-\cos^2\tfrac{1}{2}(E+\beta)}} \qquad (21)$$

For $\lambda = 0$ the last equation reduces to the well-known form

$$\sin\tfrac{1}{2}(E_0+\beta) = \nu\sin\tfrac{1}{2}\beta \qquad (22)$$

Formula (21) may be adapted to logarithmic computation by the introduction of certain auxiliary angles. Assuming a numerical value for η_1', η_1 can be found at once from (4), since c or n is supposed given. Then define an angle ψ by the relation

$$\sin\psi = n\cos\eta_1'\sec\eta_1\sin\tfrac{1}{2}\beta,$$

i. e.,

$$\sin\psi = \nu\sin\tfrac{1}{2}\beta. \qquad (23)$$

Also let $\sin\phi$ be determined by means of

$$\tan\phi = \tan c\cos\eta_1\sqrt{\sin(\tfrac{1}{2}E+\tfrac{1}{2}\beta+\psi)\sin(\tfrac{1}{2}E+\tfrac{1}{2}\beta-\psi)}\,, \qquad (24)$$

which is possible because β and D are given constants and hence $\tfrac{1}{2}E$ is obtainable from (3). Lastly, since

$$\nu^2 - 1 = \cot^2 c\sec^2\eta_1,$$

formula (21) reduces to

$$\tan\lambda = \pm\sin\phi\cot(\tfrac{1}{2}E+\tfrac{1}{2}\beta). \qquad (25)$$

In plotting the loci of constant deviation it is necessary to know the coördinates of the points of intersection with the $\lambda\eta_1'$ boundary locus. Since

$$\gamma_1 = \tfrac{1}{2}\pi \text{ or } \gamma_2' = -\tfrac{1}{2}\pi,$$

and

$$\sqrt{\nu^2 - 1} = \cot c \sec \eta_1,$$

elimination of the azimuths from equations (1), (2), (5), and (6) leads to

$$\cot c \sin \beta = 2 \cos \eta_1 \sin \tfrac{1}{2}E \sin (\beta + \tfrac{1}{2}E).$$

Combining this result with relation (3), it will be found that

$$\cos \eta_1 = \frac{2 \csc \beta \sin^2 \tfrac{1}{2}D}{\cot c \cos \beta \pm \sqrt{4 \sin^2 \tfrac{1}{2}D - \cot^2 c \sin^2 \beta}} \qquad (26)$$

Although this equation pertains directly to the $\gamma_1 \eta_1 D$ surface, it is also appropriate in this place because formula (4) gives η_1' unambiguously as soon as n and η_1 are known. Equation (26) indicates that, under suitable conditions, the loci of constant deviation will not intersect the $\lambda\eta_1'$ boundary loci or will meet each of them in two coincident points, or will intersect each in two discrete points, according as $\sin \tfrac{1}{2}D$ is less than, or equal to, or greater than $\tfrac{1}{2}\cot c \sin \beta$ respectively. Reference is made here to either half of the small-circle arcs C′AC and C′BC since everything is symmetrical with respect to the principal plane BLA. Moreover, since $\eta_1 \ngtr \tfrac{1}{2}\pi$ and $\cos \eta_1 \ngtr 1$, it does not follow that both roots of equation (26) always have physical significance. For instance, writing the radical as

$$\pm \sqrt{\cot^2 c \cos^2 \beta - (\cot^2 c - 4 \sin^2 \tfrac{1}{2}D)}$$

it is seen that the negative sign is inadmissible for

$$\cot c \leqq 2 \sin \tfrac{1}{2}D.$$

The question of what constitutes the "suitable conditions" is both important and interesting, and hence it will be discussed later. Suffice it to say, in this connection, that the case of equal roots suggests minima along the loci of greatest deviation, that is, along the $\lambda\eta_1'$ and $\gamma_1\eta_1$ boundary curves. As far as the coördinates of the points of intersection are concerned, after having calculated η_1', (indirectly), from (26) the abscissæ λ may be obtained from (9) and (10) or from (11). In the special case of equal roots

$$\sin \tfrac{1}{2}D = \tfrac{1}{2}\cot c \sin \beta, \qquad (27)$$

$$\cos \eta_1 = \tfrac{1}{2}\cot c \tan \beta. \qquad (28)$$

The intercepts of a constant deviation locus on the axes of λ and η_1' are given respectively by (21) or (25) and

$$\cos\eta_1' = (\cos^2 c \sin^2 \tfrac{1}{2}\beta + \sin^2 c \sin^2 \tfrac{1}{2}D) \csc c \csc\beta \csc\tfrac{1}{2}D. \quad (29)$$

Defining ξ by the equation

$$\tan\xi = \tan c \csc\tfrac{1}{2}\beta \sin\tfrac{1}{2}D, \quad (30)$$

the last equation changes to the logarithmic form

$$\cos\eta_1' = \cos c \sec\tfrac{1}{2}\beta \csc 2\xi. \quad (31)$$

Finally, the loci of constant deviation intersect both coördinate axes at right angles.

Before passing to the discussion of the properties of the $\gamma_1\eta_1D$ surface, a proof of a theorem relating to the internal ray (OS in figure 1) will be outlined. This theorem seems to be new, and it may be stated thus: "*When the deviation of the projected ray is kept constant, the internal ray generates a right cone with an elliptical base.*" In figure 1, let a plane be drawn tangent to the sphere of reference at the point L. Also, let L be taken as origin of a system of rectangular coördinates. The axis of x shall be the intersection of the principal plane with the tangent plane. The y-axis shall be the line common to the plane of minima, LOH, and the tangent plane. Finally, let a denote the radius of the sphere. It can now be shown that

$$\nu^2 \sin^2\lambda = \frac{x^2}{\delta^2}$$

and

$$\nu^2 \cos^2\lambda = \frac{a^2}{\delta^2},$$

where

$$\delta^2 = (x^2 + a^2)\sin^2 c - y^2 \cos^2 c.$$

Substituting in equation (20), and performing elementary transformations, it results that

$$\sin^2\tfrac{1}{2}(E+\beta)\left[\cos^2 c \cos^2\tfrac{1}{2}(E+\beta) + \sin\tfrac{1}{2}E \sin(\beta+\tfrac{1}{2}E)\right]x^2$$

$$+\cos^2 c \sin^2\tfrac{1}{2}(E+\beta)\cos^2\tfrac{1}{2}(E+\beta)y^2 =$$

$$[\sin^2 c \sin^2\tfrac{1}{2}(E+\beta) - \sin^2\tfrac{1}{2}\beta]\cos^2\tfrac{1}{2}(E+\beta)a^2 \quad (32)$$

Now

$$E + \beta = \gamma_1 - \gamma_2'$$

and

$$|\gamma_1| \leqq \tfrac{1}{2}\pi, \; |\gamma_2'| \leqq \tfrac{1}{2}\pi, \; \gamma_1 - \gamma_2' < \pi$$

hence $E + \beta < \pi$,

for all values of E having physical significance. *A fortiori*

$$\beta + \tfrac{1}{2}E < \pi,$$

consequently the coefficient of x^2 is essentially positive, as well as the coefficient of y^2. When $E=\epsilon_0$,

$$\sin^2 c \sin^2 \tfrac{1}{2}(E+\beta) - \sin^2 \tfrac{1}{2}\beta = 0,$$

by formula (19), hence the conic degenerates to the point $x=0$, $y=0$. For larger permissible values of E,

$$\sin^2 c \sin^2 \tfrac{1}{2}(E+\beta) - \sin^2 \tfrac{1}{2}\beta$$

is positive, thus giving a true ellipse and establishing the theorem stated above. Furthermore, the coefficient of x^2 is obviously greater than the coefficient of y^2, therefore the longer axis of the ellipse lies along the y-axis, *i. e.*, in the plane of minima. A consideration of the way in which E increases along a small-circle MV gives rise to the expectation of a cone of a general oval base, but the simplicity of the result was not anticipated. Conic sections were not found, by the writer, to pertain to the other rays under the various conditions which were tried.

Now that the more important properties of the $\lambda\eta_1{}' D$ surface have been presented, it is appropriate to discuss the $\gamma_1\eta_1 D$ locus. The problem of the internal ray was taken up first because of the simplicity and symmetry of the results obtained. In spite of the comparatively complicated nature of the $\gamma_1\eta_1 D$ surface it is the more interesting because it shows the dependence of the general deviation upon the azimuth and altitude of the incident ray. This added interest rests partly on the fact that it seems natural to consider the incident ray in all permissible positions, around a fixed point of incidence, and to investigate the corresponding values of the deviation.

From (2),

$$\cos E = \cos(\gamma_1-\beta)\cos\gamma_2{}' + \sin(\gamma_1-\beta)\sin\gamma_2{}'.$$

From (1) and (6),

$$\sin\gamma_2{}' = \nu\sin(\gamma_1{}'-\beta),$$

hence, using (5) and observing that $\gamma_1{}' \not> \tfrac{1}{2}\pi$, it will be found that

$$\sin\gamma_2{}' = \cos\beta\sin\gamma_1 - \sin\beta\sqrt{\nu^2-\sin^2\gamma_1}\ .$$

Since $\gamma_2{}' \not> \tfrac{1}{2}\pi$,

$$\cos\gamma_2{}' = +\sqrt{1-\sin^2\gamma_2{}'},$$

therefore

$$\cos E = \sin(\gamma_1-\beta)\left[\cos\beta\sin\gamma_1 - \sin\beta\sqrt{\nu^2-\sin^2\gamma_1}\right]$$
$$+\cos(\gamma_1-\beta)\sqrt{1-\left[\cos\beta\sin\gamma_1-\sin\beta\sqrt{\nu^2-\sin^2\gamma_1}\right]^2} \qquad (33)$$

From (3),

$$\cos D = \sin^2 \eta_1 + \cos^2 \eta_1 \cos E,$$

so that substitution in (33) with due attention to (4), gives

$$\begin{aligned}\cos D = {} & \sin^2 \eta_1 + \cos \eta_1 \sin (\gamma_1 - \beta) [\cos \beta \sin \gamma_1 \cos \eta_1 \\ & - \sin \beta \sqrt{\cot^2 c + \cos^2 \gamma_1 \cos^2 \eta_1}] + \cos \eta_1 \cos (\gamma_1 - \beta) \times \\ & \sqrt{\cos^2 \eta_1 - [\cos \beta \sin \gamma_1 \cos \eta_1 - \sin \beta \sqrt{\cot^2 c + \cos^2 \gamma_1 \cos^2 \eta_1}]^2} \qquad (34)\end{aligned}$$

This is the general formula for the $\gamma_1 \eta_1 D$ surface, it being understood that D is always positive. The last equation may also be written

$$\begin{aligned}\sin \tfrac{1}{2} D = {} & \\ \tfrac{1}{2} \Big\{ & \sqrt{\cos \eta_1 [1 + \sin (\gamma_1 - \beta)] \{ [1 - \sin (\gamma_1 - \beta)] \cos \eta_1 + u \sin \beta \}} \\ & - \sqrt{\cos \eta_1 [1 - \sin (\gamma_1 - \beta)] \{ [1 + \sin (\gamma_1 - \beta)] \cos \eta_1 - u \sin \beta \}} \Big\} \qquad (35)\end{aligned}$$

where

$$u = \sqrt{\cot^2 c + \cos^2 \gamma_1 \cos^2 \eta_1} - \cos \gamma_1 \cos \eta_1 .$$

Since $\eta_1 \not> \tfrac{1}{2}\pi$, the expression under the first long radical is always positive. The second long radical will become imaginary when

$$(1 + \cos \beta \sin \gamma_1) \cos \eta_1 < \sin \beta \sqrt{\cot^2 c + \cos^2 \gamma_1 \cos^2 \eta_1} ,$$

therefore the equation of the left boundary of the $\gamma_1 \eta_1 D$ surface may be written

$$\sin \gamma_1 \cos \eta_1 + \cos \beta \cos \eta_1 = \cot c \sin \beta \qquad (36)$$

[The unrationalized form of (36) can be obtained directly by combining the condition $\gamma_2' = -\tfrac{1}{2}\pi$ with (1), (5), and (6). Also, along the left boundary locus formulæ (33) and (35) reduce to $E = \tfrac{1}{2}\pi + \gamma_1 - \beta$ and $\sin \tfrac{1}{2} D = \sin \tfrac{1}{2}(\tfrac{1}{2}\pi + \gamma_1 - \beta) \cos \eta_1$, as they should do, conformably to (2) and (3).] Combining the last equation with (28) it will be found that

$$\gamma_1 = \tfrac{1}{2}\pi - \beta$$

and therefore

$$E = \pi - 2\beta.$$

Assuming, for the time being, (since it will be formally demonstrated later), that the case of equal roots, characterized by (27) and (28), corresponds to discrete minima on the boundary loci, the following theorem, which seems to be new, may now be stated: "*At the discrete minima on the boundary loci of the* $\gamma_1\eta_1 D$ *surface the deviation of the projected ray is the supplement of twice the prism angle.*" In calculating the coördinates of points on the left boundary of the $\gamma_1\eta_1 D$ surface, it is convenient to assume γ_1 and to derive η_1 from the following modified form of (36), namely:

$$\cos\eta_1 = \tfrac{1}{2}\cot c\sin\beta\csc\tfrac{1}{2}(\tfrac{1}{2}\pi-\beta+\gamma_1)\sec\tfrac{1}{2}(\tfrac{1}{2}\pi-\beta-\gamma_1) \qquad (37)$$

The right boundary is simply $\gamma_1 = \frac{1}{2}\pi$.

The following special cases will be found useful. For grazing incidence or grazing emergence formula (35) reduces to

$$\sin\tfrac{1}{2}D = \tfrac{1}{2}\sin\beta\sqrt{\cos\eta_1}\left\{\sqrt{\cos\eta_1+\cot c\cot\tfrac{1}{2}\beta} - \sqrt{\cos\eta_1-\cot c\tan\tfrac{1}{2}\beta}\right\} \qquad (38)$$

For $\eta_1 = 0$ formula (38) reduces to (16). For grazing emergence in a principal plane (36) gives

$$\sin\gamma_1 = \csc c\sin(\beta-c) \qquad (39)$$

For simultaneous grazing incidence and emergence (36) leads to

$$\left.\begin{aligned}\cos\eta_1 &= \cot c\tan\tfrac{1}{2}\beta\\ \text{or}\quad \tan\tfrac{1}{2}\eta_1 &= \pm\sqrt{\csc(c+\tfrac{1}{2}\beta)\sin(c-\tfrac{1}{2}\beta)},\end{aligned}\right\} \qquad (40)$$

and (38) becomes (15). Anywhere along the left boundary

$$\frac{d\eta_1}{d\gamma_1} = \tan c\csc\beta\cos\gamma_1\cos\eta_1\cot\eta_1,$$

hence this locus crosses the γ_1-axis, and also intersects the right boundary, at right angles. The intercepts on the η_1-axis of the left boundary may be derived at once from (36). They are given by

$$\left.\begin{aligned}\cos\eta_1 &= \cot c\tan\beta\\ \text{or}\quad \tan\tfrac{1}{2}\eta_1 &= \pm\sqrt{\csc(c+\beta)\sin(c-\beta)}.\end{aligned}\right\} \qquad (41)$$

Then (35) simplies to

$$\sin\tfrac{1}{2}D = \cot c\tan\beta\sin\tfrac{1}{2}(\tfrac{1}{2}\pi-\beta) \qquad (42)$$

In order that these intersections may be real and discrete, and that γ_1 may have negative values, the necessary and sufficient condition is $\beta < c$.

For normal incidence or emergence formulæ (8) and (34) each lead to

$$\sin(D+\beta) = \csc c\sin\beta \qquad (43)$$

In the case of the $\lambda\eta_1' D$ surface, equation (8) was not used to calculate the coördinates of the points of the constant deviation loci because of the involved nature of (8). Instead, formula (25) was derived, and the manner of using it for numerical calculations was explained. For the same reason equations (34) and (35) are not convenient for calculating the constant deviation sections of the $\gamma_1\eta_1 D$ surface. Furthermore, it is not desirable to attempt to transform (21) or (25) from the $\lambda\eta_1'$ coördinates to the $\gamma_1\eta_1$ system, since the equations of transformation suggest that a very complicated function of γ_1 in terms of η_1 and D would result. For, the equations of transformation may be written,

$$\sin\lambda = [\cos\tfrac{1}{2}\beta\sin\gamma_1\cos\eta_1 - \sin\tfrac{1}{2}\beta\sqrt{\cot^2 c + \cos^2\gamma_1\cos^2\eta_1}]\times(\cot^2 c + \cos^2\eta_1)^{-½}$$

and

$$\sin\eta_1' = \sin c\sin\eta_1.$$

A much simpler plan is to assume values for D and η_1, and then calculate E and η_1' by means of (3) and (4) respectively. Next evaluate λ and hence γ_1' from (25), and finally get γ_1 from (5).

Although it can be established by analysis that each locus of constant deviation has an algebraic maximum, (η_1 positive), and a like minimum, (η_1 negative), at points on the $\gamma_1\eta_1$ plane of projection which correspond to $\lambda = 0$, ($\gamma_1' = \frac{1}{2}\beta$), nevertheless this property seems to be self-evident, and therefore, the formal demonstration will be omitted. The equation of the projection on the $\gamma_1\eta_1$ plane of the locus of these stationary points may be written

$$\sin^2\gamma_1\cos^2\eta_1 - \sin^2\tfrac{1}{2}\beta\cos^2\eta_1 = \cot^2 c\sin^2\tfrac{1}{2}\beta \qquad (44)$$

Hence, the coördinates of points on this curve may be readily obtained by assuming values for γ_1 and calculating η_1 from

$$\cos\eta_1 = \cot c\sin\tfrac{1}{2}\beta\sqrt{\csc(\gamma_1 + \tfrac{1}{2}\beta)\csc(\gamma_1 - \tfrac{1}{2}\beta)} \qquad (45)$$

Along the projected locus,

$$\frac{d\eta_1}{d\gamma_1} = \sec c\tan c\csc\tfrac{1}{2}\beta\cos\gamma_1\cos\eta_1\cot\eta_1\cos\eta_1'$$

hence it intersects both the γ_1-coördinate axis and the right boundary locus normally. The absolute minimum, ϵ_0, falls at the point

$$\left.\begin{aligned}\gamma_1 &= \sin^{-1}(\csc c\sin\tfrac{1}{2}\beta),\\ \eta_1 &= 0.\end{aligned}\right\} \qquad (46)$$

For $\lambda = 0$ formula (8) may be transformed into

$$\sin\tfrac{1}{2}D = \{\sqrt{(\cot^2 c + \cos^2\eta_1)\cos^2\tfrac{1}{2}\beta} - \sqrt{(\cot^2 c + \cos^2\eta_1)\cos^2\tfrac{1}{2}\beta - \cot^2 c}\}\sin\tfrac{1}{2}\beta* \qquad (47)$$

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* H. S. Uhler, this Journal, vol. xxvii, p. 227, 1909.

Attention will now be directed to the interesting problem of the variation of the deviation at grazing incidence, that is, along the right boundary locus. Formula (38) may be written

$$\sin \tfrac{1}{2}D = \tfrac{1}{2} \sin \beta(R_1 - R_2) \sqrt{\cos \eta_1},$$

where

$$R_1 = \sqrt{\cos \eta_1 + \cot c \cot \tfrac{1}{2}\beta}$$

and

$$R_2 = \sqrt{\cos \eta_1 - \cot c \tan \tfrac{1}{2}\beta.}$$

It follows that

$$\frac{dD}{d\eta_1} = (R_1 R_2)^{-1} \tan \tfrac{1}{2}D \tan \eta_1 (\cos \eta_1 - R_1 R_2).$$

In general, therefore, stationary values of D may correspond to

$$\eta_1 = 0$$

and

$$\cos \eta_1 - R_1 R_2 = 0,$$

the latter being equivalent to

$$\cos \eta_1 = \tfrac{1}{2} \cot c \tan \beta,$$

which is relation (28). It is easy to show that

$$\frac{d^2D}{d\eta_1^{\,2}} = \tfrac{1}{2}(R_1 R_2)^{-3} \csc^2\beta \tan \tfrac{1}{2}D \{4 \sin \eta_1 \tan \eta_1 \sin^2 \tfrac{1}{2}D +$$
$$R_1 R_2 \Theta [\Theta \sec^2 \tfrac{1}{2}D \tan^2 \eta_1 + 2 \sin \eta_1 \tan \eta_1 + 2 R_1 R_2 \sec^2 \eta_1] \sin^2 \beta\}$$

where $\Theta = \cos \eta_1 - R_1 R_2$, therefore

$$\left(\frac{d^2D}{d\eta_1^{\,2}}\right)_{\eta_1 = 0} = \{[1 + (2 \tan c - \tan \beta) \cot^2 c \cot \beta]^{-\frac{1}{2}} - 1\} \tan \tfrac{1}{2}D =$$
$$[\sin c \sqrt{\sin \beta \csc (2c - \beta)} - 1] \tan \tfrac{1}{2}D,$$

and

$$\left(\frac{d^2D}{d\eta_1^{\,2}}\right)_{\Theta = 0} = 2 \sin^2 \tfrac{1}{2}D \tan \tfrac{1}{2}D \csc^2 \beta \sec^2 \eta_1 \tan^2 \eta_1.$$

Assuming β acute, $\left(\frac{d^2D}{d\eta_1^{\,2}}\right)_{\eta_1 = 0}$ is positive or negative, according as $\tan \beta > 2 \tan c$ or $\tan \beta < 2 \tan c$, hence the deviation at grazing incidence in a principal plane is a maximum when $\tan \beta < 2 \tan c$, and a minimum when $\tan \beta > 2 \tan c$. Again, when $\cos \eta_1 = \tfrac{1}{2}\cot c \tan \beta$ and $\eta_1 \lesseqgtr 0$, $\left(\frac{d^2D}{d\eta_1^{\,2}}\right)_{\Theta = 0}$ is essentially positive so that the deviation experiences a minimum value. Since $\cos(+\eta_1) = \cos(-\eta_1)$ there will be two minima at grazing incidence corresponding to $\Theta = 0$. Moreover, since the cosine of any angle may not exceed unity in magnitude it is evident that these minima will exist when, and only when, $\tan\beta < 2\tan c$, that is, simultaneously with the aforementioned maximum in the principal plane. The case where $\tan\beta = 2\tan c$ requires special investigation, for then $\left(\frac{d^2D}{d\eta_1^{\,2}}\right)_{\Theta=\eta_1=0}$ vanishes. Keeping c or n constant and allowing β to vary in the equation $\cos\eta_1 = \frac{1}{2}\cot c\tan\beta$ it is seen that when $\beta = 0$, $\eta_1 = \frac{1}{2}\pi$, and that as β increases, η_1 decreases and approaches the limit 0 as β approaches the value $\tan^{-1}(2\tan c)$. Since *two* minima are moving in symmetrically towards *one* maximum of fixed position, it seems reasonable to expect a resultant minimum, of higher order than the first, when the limiting condition $\tan\beta = 2\tan c$ is fulfilled. By comparatively laborious but elementary analysis it can be shown that $\frac{d^3D}{d\eta_1^{\,3}}$ vanishes for $\eta_1 = 0$, and that

$$\frac{d^4D}{d\eta_1^{\,4}} = 12\cos^2\beta\cot^2\beta\csc D$$

when

$$\Theta = \eta_1 = 0,\ i.\ e.,$$

$$\tan\beta = 2\tan c \qquad (48)$$

This result being positive the expectation of a minimum, of higher order than the first, is realized. The expression under the radical of $\left(\frac{d^2D}{d\eta_1^{\,2}}\right)_{\eta_1=0}$ may also be written

$$1 - \cot^2 c + 2\cot c\cot\beta$$

hence, (assuming $2c$ obtuse so as to permit β to become obtuse and still satisfy the necessary condition $\beta < 2c$), as β increases from a very small value up to $\tan^{-1}(2\tan c)$, exclusive of this limit, $\left(\frac{d^2D}{d\eta_1^{\,2}}\right)_{\eta_1=0}$ maintains a negative value so that a maximum of deviation persists. When $\beta = \tan^{-1}(2\tan c)$, (which implies β acute), it has been shown that the deviation is a minimum. The instant β exceeds $\tan^{-1}(2\tan c)$, $\left(\frac{d^2D}{d\eta_1^{\,2}}\right)_{\eta_1=0}$ becomes positive and remains so while β increases to $\frac{1}{2}\pi$, passes through $\frac{1}{2}\pi$, and continues obtuse up to the limit $2c$. To sum up, *there is one minimum for* $\gamma_1 = \frac{1}{2}\pi$ *when* $2c > \beta \overset{=}{>} \tan^{-1}(2\tan c)$, *whereas there are discrete minima and one maximum when*

$$\tan^{-1}(2\tan c) > \beta > 0.$$

For a given value of η_1 the deviation on the left boundary is obviously the same as the deviation on the right boundary. On the other hand, the corresponding abscissæ are

$$\gamma_1 = \sin^{-1}(\cot c \sin\beta \sec\eta_1 - \cos\beta),$$

and $$\gamma_1 = \tfrac{1}{2}\pi. \qquad \text{[See formula (36)]}$$

At the discrete minima

$$\sec\eta_1 = 2\tan c \cot\beta$$

hence $$\gamma_1 = \tfrac{1}{2}\pi - \beta,$$

as was obtained before in the case of equal roots of equation (26). Thus, as expected, the equal roots pertain to the discrete minima, four in all. Also, *the azimuth of the incident ray is the complement of the prism angle for the two discrete minima of deviation corresponding to grazing emergence.* [At the four minima it was shown earlier that $E = \pi - 2\beta$.]

The value of the deviation at the discrete minima is given by formula (27). When $\tan\beta = 2\tan c$, that is, when the discrete minima coalesce with their respective maxima, the deviation too is the supplement of twice the prism angle.

The case of two discrete minima and one maximum suggests that it may be possible for the deviation at grazing incidence in a principal plane to equal the deviation at simultaneous grazing incidence and emergence. Moreover, since, for a given altitude η_1, the greatest deviations correspond to the small-circle boundaries (U and V of fig. 1), the problem just suggested is very closely related to the question of the location of the greatest deviation which can be produced by a prism of given angle and relative index of refraction. A very incomplete attempt to investigate the greatest deviation has been made by A. Anderson in a paper* entitled: "On the Maximum Deviation of a Ray of Light by a Prism."

Let D_1 denote the deviation for grazing incidence in a principal plane and D_2 the deviation for simultaneous grazing incidence and emergence. A fruitful formula involving $D_1 - D_2$ will now be derived. Equation (17) may be written

$$\cos(D_1 + \beta) = \cos\beta - 2\cot c \sin\tfrac{1}{2}\beta \cos\tfrac{1}{2}\beta.$$

The formula

$$\cos(D_2 + \beta) = \cos\beta \cos D_2 - \sin\beta \sin D_2$$

becomes

$$\cos(D_2 + \beta) = \cos\beta - 2\cot^2 c \cos\beta \sin^2\tfrac{1}{2}\beta - 2\cot c \sin\beta \sin\tfrac{1}{2}\beta \sqrt{1 - \cot^2 c \sin^2\tfrac{1}{2}\beta},$$

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* Proc. Camb. Phil. Soc., vol. ix, p. 195, 1898.

since, by (15),

$$\sin \tfrac{1}{2}D_2 = \cot c \sin \tfrac{1}{2}\beta.$$

Hence

$$\cos (D_1 + \beta) - \cos (D_2 + \beta) = 2 \cot c \sin \tfrac{1}{2}\beta \times$$
$$\left\{\cot c \cos \beta \sin \tfrac{1}{2}\beta - \cos \tfrac{1}{2}\beta + \sin \beta \sqrt{1 - \cot^2 c \sin^2 \tfrac{1}{2} \beta}\right\}$$

or

$$\sin \tfrac{1}{2}(D_1 - D_2) = \cos c \sin \tfrac{1}{2}\beta \left\{\sin (c - \tfrac{1}{2}\beta) + 2 \cos c \sin^3 \tfrac{1}{2}\beta\right.$$
$$\left. - \sin \beta \sqrt{\sin^2 c \sin^2 \tfrac{1}{2}\beta + \sin^2 c - \sin^2 \tfrac{1}{2}\beta}\right\} \div$$
$$\sin^2 c \sin[\tfrac{1}{2}(D_1 + D_2) + \beta]$$

Obviously, the quantity within the braces may be rationalized by multiplying by

$$\sin (c - \tfrac{1}{2} \beta) + 2 \cos c \sin^3 \tfrac{1}{2}\beta$$
$$+ \sin \beta \sqrt{\sin^2 c \sin^2 \tfrac{1}{2}\beta + (\sin^2 c - \sin^2 \tfrac{1}{2}\beta)}.$$

Since c cannot be less than $\tfrac{1}{2} \beta$ each term of the last expression is real and positive, so that the fraction which equals $\sin \tfrac{1}{2} (D_1 - D_2)$ will not be made indeterminate or ambiguous by multiplying both numerator and denominator by the rationalizing factor. Denoting the reciprocal of this factor by κ^2, for brevity, it will be found that

$$\sin \tfrac{1}{2} (D_1 - D_2) = \kappa^2 \cot c \sin \tfrac{1}{2}\beta \sin (c - \tfrac{1}{2}\beta) \times$$
$$\csc [\tfrac{1}{2} (D_1 + D_2) + \beta] (\cos \tfrac{3}{2}\beta - \cot c \sin \tfrac{1}{2}\beta) \qquad (49)$$

Now

$$\pi - \beta > D_1 > 0$$

and

$$\pi - \beta > D_2 > 0,$$

hence

$$\tfrac{1}{2} (D_1 + D_2) + \beta < \pi$$

or

$$\sin [\tfrac{1}{2} (D_1 + D_2) + \beta] > 0,$$

for all cases except the trivial, extreme case where $\beta = 2c$. Hence, in general,

$$\sin (c - \tfrac{1}{2}\beta) \csc [\tfrac{1}{2} (D_1 + D_2) + \beta]$$

is positive and determinate. Therefore, *the deviation at grazing incidence in a principal plane* (D_1) *is greater than, or equal to, or less than, the deviation at simultaneous grazing incidence and emergence* (D_2), *according as* $\cos \tfrac{3}{2}\beta$ *is greater than, or equal to, or less than*, $\cot c \sin \tfrac{1}{2}\beta$, *respectively.* For all practical purposes, this answers the question concerning the location of the greatest deviation produced by a prism of specified constants. The equation

$$\cos \tfrac{3}{2}\beta = \cot c \sin \tfrac{1}{2}\beta, \tag{50}$$

which is the necessary and sufficient condition for $D_1 = D_2$, shows that *the deviation at grazing incidence in a principal plane can never equal the deviation at simultaneous grazing incidence and emergence for a prism having an angle greater than* $\frac{1}{3}\pi$, *regardless of the value of the index of refraction.* For, let the curves whose equations are $y = \cos \frac{3}{2}\beta$ and $y = \cot c \sin \frac{1}{2}\beta$ be plotted on the same diagram, with the values of β as abscissæ. As β increases from zero, the curve $y = \cos \frac{3}{2}\beta$ will commence with the intercept 1 on the y-axis and will have decreasing positive ordinates until it crosses the β-axis at the intercept $\beta = \frac{1}{3}\pi$. On the other hand, assuming c given, the curve $y = \cot c \sin \frac{1}{2}\beta$ will begin at the origin and have increasing positive ordinates, as β increases, until $\beta = \pi$. Therefore, the abscissa of the point of intersection of these curves must be less than $\frac{1}{3}\pi$, save in the trivial case where $\cot c = 0$ or $n = 1$. In this extreme case the point of intersection is $(\frac{1}{3}\pi, 0)$. It is also evident that the larger the value of $\cot c$, (or n), the smaller will be the value of β corresponding to $D_1 = D_2$. When c is given and the prism angle which will make the deviations D_1 and D_2 equal is required, it will be found convenient to transform equation (50) to a function of $\frac{1}{2}\beta$ alone. Denoting $\tan \frac{1}{2}\beta$ by t, the last equation may be reduced to the following cubic

$$\cot c \,.\, t^3 + 3t^2 + \cot c \,.\, t - 1 = 0 \tag{51}$$

Equation (51) always has one positive real root because $\cot c$ is positive and the constant term is negative. Moreover, it can only have one positive root in accordance with the "Rule of Signs" of Descartes. Since $\pi > \beta > 0$, t must be positive so that there is no ambiguity in the solution of the cubic. Writing the left-hand member of (51) as

$$t\,(1 + t^2) \cot c - (1 - 3t^2),$$

and observing that t must be positive, it becomes clear that $1 - 3t^2$ must be positive to make the expression vanish. This amounts to a second proof that β must not exceed $\frac{1}{3}\pi$ in order to make possible the equality of D_1 and D_2.

It seems appropriate, at this stage of the discussion, to direct attention to the illustrative figures and numerical data. The chalk lines reproduced in fig. 1 represent roughly the following theoretical values: $\beta = 20°$, $n = 1{\cdot}5$, $c = \cot^{-1}\sqrt{n^2 - 1} = \angle \mathrm{N_1OA} = \angle \mathrm{N_2OB} = 41° 48' 37''$, $a_1 = 55° 57' 45''$, $a_1' = 33°$

FIGS. 2–6.

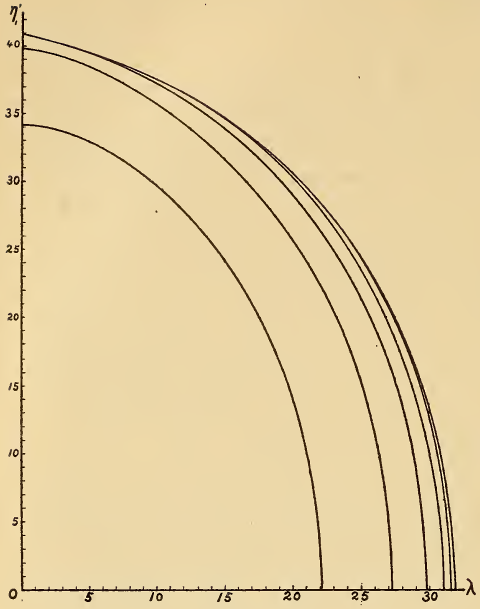


FIG. 2.

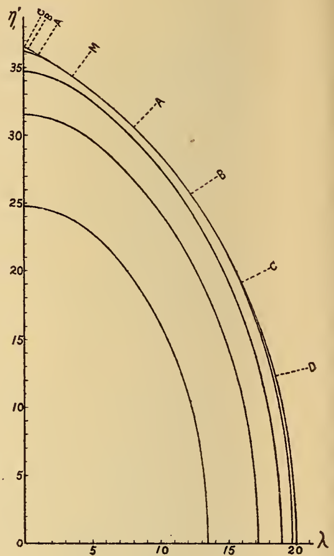


FIG. 3.

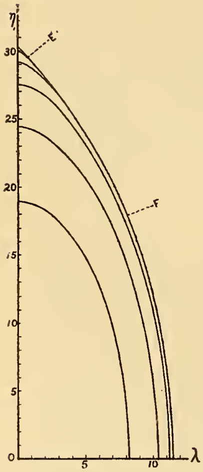


FIG. 4.

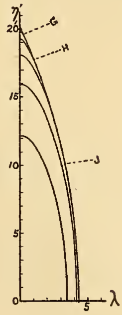


FIG. 5.

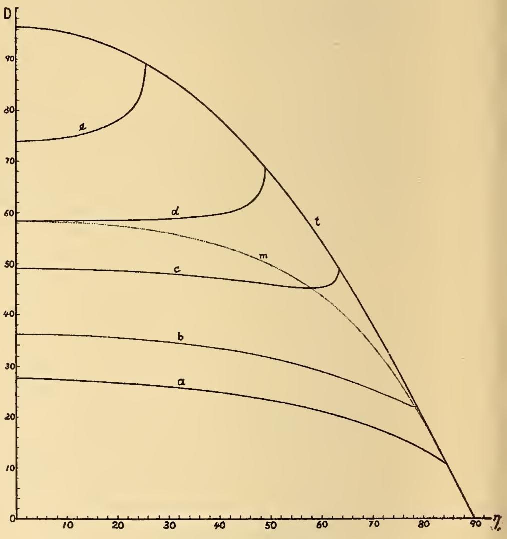


FIG. 6.

32′ 6″, $a_2 = 21° 18′ 17″$, and $a_2' = 33° 1′ 26″$. The a's may be calculated by the aid of the following relations:

$$\cos a_1 = \cos \gamma_1 \cos \eta_1 \tag{52}$$

$$\cos a_2' = \cos \gamma_2' \cos \eta_1 \tag{53}$$

$$\sin a_1' = \sin c \sin a_1 \tag{54}$$

$$\sin a_2 = \sin c \sin a_2' \tag{55}$$

$\eta_1 = \eta_2' = 30° 51′ 57″$, $\eta_1' = 20°$, $\gamma_1 = 49° 18′ 2″$, $\gamma_1' = 27° 29′ 46″$, $\gamma_2 = 7° 29′ 46″$, $\gamma_2' = 12° 22′ 12″$, $D = 14° 31′ 7″$, and $E = 16° 55′ 50″$. The absolute minimum of deviation, which is attained when S coincides with L, $\epsilon_0 = 10° 11′ 46″$. The partial minimum corresponding to the altitude LM, when S falls on M, $D_0 = \angle Q_0OP_0 = 11° 16′ 7″$. The associated deviation for the projected ray, $E_0 = 13° 8′ 8″$. The deviation at grazing incidence or emergence in a principal plane, when P coincides with K or R, $D_1 = 36° 7′ 50″$. $\angle N_1OK = \angle N_1OT = 90°$, and $\angle N_1OR = -33° 52′ 10″$. The deviation for simultaneous grazing incidence and emergence, when P and S coincide respectively with T and C, $D_2 = 22° 23′ 22″$. $\angle KOT = 78° 37′ 49″$. When referred to rectangular frames the small-circle arcs C′AC and C′BC have been called respectively the right and left boundary loci of the $\lambda\eta_1'D$ surface. In like manner, the great-circle arc T′KT and the curve T′RT have been designated as the right and left boundary loci of the $\gamma_1\eta_1D$ surface, in the order named. T′ being the point homologous to T. The course of the curve TR does not show very well in the photograph. When viewed from above, in the direction $\overrightarrow{HO}$, it is seen to recede more and more from H as the tracing point starts from T and moves towards R.

Figures 2 to 5, inclusive, show the projections on the $\lambda\eta_1'$ coördinate plane of certain constant deviation sections of the $\lambda\eta_1'D$ surfaces. Only the first quadrant is plotted for each locus since all of the sections are symmetrical with respect to both of the axes $\overline{O\lambda}$ and $\overline{O\eta_1'}$. The complete boundary loci of the $\lambda\eta_1'D$ surfaces are cylinders whose generating lines are parallel to the axes $\overline{OD}$ and hence perpendicular to the plane of the paper. For this reason any one quadrant of each boundary locus projects on the $\lambda\eta_1'$ plane as a single curve which may be intersected by any number of loci of constant deviation. The boundary loci arise from the physical condition that total reflection is to be excluded. There is nothing inherent in the mathematical functions to prevent the loci of constant deviation, or any other sections of the $\lambda\eta_1'D$ surfaces which intersect the boundary loci, from being plotted continuously so as to include points in the region outside of the bounding cylinders, that is, beyond the convex sides of these cylinders. However, in figures 2 to 5 the loci of constant deviation have not been plotted beyond the boundary loci. The relative index of refraction has been given the value 1·5 throughout. Each figure corresponds to a different value of the prism angle, (β), so that the group of figures taken collectively shows how the dimensions of the $\lambda\eta_1'D$ surface depend upon the angle of the prism. To facilitate comparison, figures 2 to 5 are drawn to the same scale. The values of β pertaining to figures 2, 3, 4, and 5 are, respectively, 20°, 43° 37′ 58″, 60° 47′ 39″, and 75°. The angles 20° and 75° were chosen arbitrarily as being relatively small and large. On the other hand, with $n = 1{\cdot}5$, $\beta = 43° 37' 58''$ illustrates the case of equality between the deviation at grazing incidence in a principal plane and the deviation at simultaneous grazing incidence and emergence. This value of β was derived from the cubic equation (51). Figure 4 illustrates the special case in which the two minima of deviation at grazing incidence coalesce with the maximum of deviation at grazing incidence in a principal plane. The angle of the prism was calculated from condition (48), namely, $\tan \beta = 2 \tan c$. The acute angles which the boundary loci make with the $\eta_1'D$ coördinate planes equal 78° 27′ 34″, 61° 40′ 18″, 44° 47′ 29″, and 25° 24′ 55″ for figures 2, 3, 4, and 5, respectively. The successive increments of deviation from one locus of constant deviation to the next are kept constant for each diagram, but the value of this constant difference is not the same for all four figures. More precisely, for each of the figures, 2, 4, and 5, the value of ϵ_0 was subtracted from the value of the greatest possible deviation, (D_1 or D_2), and this difference was divided by 6. This accounts for the presence of minutes and seconds of arc in the deviations in these families. In figure 3 the five increments of deviation are practically constant. They have the values 4° 52′ 25″, 5° 0′ 0″, 5° 0′ 0″, 5° 0′ 0″, and 5° 6′ 6″. Hence, for each family of curves, the relatively great distance of the innermost locus of constant deviation from the origin and the crowding together of the constant deviation loci near the boundary curve show how the steepness of the $\lambda\eta_1'D$ surface increases as the deviation exceeds the value of the absolute minimum by ever increasing amounts. The values of the most important quantities pertaining to the four families of constant deviation loci are collected in Table I.

A few additional points deserve notice. For $\beta = 20°$ the minimum of all deviations along the boundary locus has the value 22° 2′ 42″, and the coördinates $\lambda = 0° 18' 51''$ and $\eta_1' = 40° 44' 50''$. Hence, only within the small interval (22° 23′ 22″) $-$(22° 2′ 42″) $=$ 0° 20′ 40″ is it possible for the curves of con-

TABLE I.

β	Families, D	Intercept, λ-axis.	Intercept, η_1'-axis.	Boundary intersections		Extreme values.
				λ	η_1'	
20° 0′ 0″	14° 31′ 7″	22° 5′ 2″	34° 8′ 1″			ε_0 = 10° 11′ 46″ D_1 = 36 7 50 λ = 31 48 37 D_2 = 22 23 22 η_1' = 40 48 44
	18 50 27	27 15 1	39 50 1			
	23 9 48	29 46 12	beyond boundary	2° 47′ 45″	40° 9′ 6″	
	27 29 9	31 2 58	“	11 0 31	37 1 9	
	31 48 29	31 38 34	“	20 49 53	29 46 10	
43° 37′ 58″	29 0 0	13 28 53	24 45 40			ε_0 = 24 7 35 D_1 = 49 6 5 λ = 19 59 38 D_2 = 49 6 5 η_1' = 36 35 46
	34 0 0	17 9 20	31 27 56			
	39 0 0	18 56 27	34 41 50			
	44 0 0	19 45 48	36 10 47			
60° 47′ 39″	43 6 49	8 14 52	18 56 15			ε_0 = 37 57 20 D_1 = 58 24 43 λ = 11 24 48 D_2 = 68 54 13 η_1' = 30 12 55
	48 16 18	10 19 49	24 29 5			
	53 25 46	11 12 7	27 29 35			
	58 35 15	beyond boundary	29 9 38	F; 8 3 21	17 51 57	
	63 44 44	“	29 58 50	E; 0 39 7	29 32 28	
75° 0′ 0″	61 42 9	3 28 55	12 12 16			ε_0 = 56 53 11 D_1 = 70 11 49 λ = 4 18 37 D_2 = 85 47 1 η_1' = 20 1 56
	66 31 8	4 11 20	15 57 9			
	71 20 6	beyond boundary	18 3 17	J; 3 17 58	10 3 41	
	76 9 4	“	19 15 10	H; 1 0 30	17 43 39	
	80 58 3	“	19 51 23	G; 0 11 27	19 37 25	

stant deviation to intersect the boundary in two discrete points. Thus for $D = 22° 13' 2''$ the close intersections with the boundary locus are given by $\lambda = 0° 57' 19''$, $\eta_1' = 40° 36' 25''$, and $\lambda = 0° 1' 34''$, $\eta_1' = 40° 48' 25''$. In order to show the distribution of deviation along the boundary locus of figure 3 the following numerical data have been calculated. [This distribution is shown in another way in figure 6.] At M the deviation has the minimum value 45° 22′ 46″, with the coördinates $\lambda = 3° 40' 13''$, $\eta_1' = 34° 20' 22''$. At the points AA, $D = 46°$, $\lambda = 8° 12' 47''$ with $\eta_1' = 30° 34' 48''$ and $\lambda = 1° 9' 18''$ with $\eta_1' = 35° 56' 52''$. At BB, $D = 47°$, $\lambda = 12° 21' 20''$ with $\eta_1' = 25° 43' 29''$, and $\lambda = 0° 21' 36''$ with $\eta_1' = 36° 23' 59''$. At CC, $D = 48°$, $\lambda = 16° 4' 5''$ with $\eta_1' = 19° 11' 55''$ and $\lambda = 0° 4' 39''$ with $\eta_1' = 36° 33' 16''$. For $D = 48° 40'$ the point D is given by $\lambda = 18° 27' 26''$ with $\eta_1' = 12° 20' 3''$. The upper intersection, which could not be plotted, has the coördinates $\lambda = 0° 0' 38''$ and $\eta_1' = 36° 35' 26''$

Figure 6 pertains to the $\gamma_1\eta_1D$ surface in that it shows the dependence of the deviation at grazing incidence upon the altitude η_1 and the prism angle β. Each of the curves **a**, **b**, **c**, **d**, and **e** is characterized by a different value of β, and also each curve represents the intersection of the plane $\gamma_1 = 90°$ with the corresponding $\gamma_1\eta_1 D$ surface. In other words, for the chosen values of the prism angle, figure 6 shows the distribution of deviation along the great-circle arc KT of figure 1. As before, $n = 1{\cdot}5$. The values of β for the curves **a**, **b**, **c**, **d**, and **e** are 9° 42′, 20°, 43° 37′ 58″, 60° 47′ 39″, and 77° 42′, in the order named. The ordinate of each point along the coördinate axis $\overline{\mathrm{OD}}$ signifies the deviation at grazing incidence in a principal plane corresponding to the associated value of the prism angle. That is, the line $\overline{\mathrm{OD}}$ is the locus of D_1 when β varies. From the same point of view, the complete curve **t** passes through all points pertaining to simultaneous grazing incidence and emergence, or, it is the locus of D_2 when β assumes all possible values. The greatest value of the prism angle consistent with transmission is given by $\beta = 2c$. In this limiting case the only ray possible corresponds to simultaneous grazing incidence and emergence in a principal plane, $\epsilon_0 = D_1 = D_2 = 180° - 2c$, the $\lambda\eta_1'D$ and $\gamma_1\eta_1 D$ surfaces degenerate into single points, and the small-circle arcs of figure 1 become tangent, so that A and B coincide. For $n = 1{\cdot}5$ the limiting values are $\beta = 83° \ 37' \ 14''$ and $D = 96° \ 22' \ 46''$. Figure 6 shows very clearly that the greatest deviation which can be produced by a prism having a given index of refraction is obtained when $\beta = 2c$. This follows from the fact that when both β and c are fixed the greatest deviation corresponds to grazing incidence, and figure 6 has $\gamma_1 = 90°$ and $c = constant$ throughout. [See pages 393 and 405.] For the curves **a, b,** and **c,** β is less than $\tan^{-1}(2 \tan c)$, hence each complete locus has two discrete minima and one maximum which corresponds to grazing incidence in a principal plane. [Only one-half of each curve is shown in the figure since $\overline{\mathrm{OD}}$ is the axis of symmetry.] The line **c** satisfies condition (50), namely,

$$\cos \tfrac{3}{2}\beta - \cot c \sin \tfrac{1}{2}\beta = 0,$$

hence the ordinates at the extremities of the plotted curve are equal, ($D_1 = D_2$). The condition $\tan \beta = 2 \tan c$ is fulfilled by curve **d**, hence the discrete minima coincide with the maximum and produce a resultant minimum in the principal plane. Thus, as β increases from 0, the curve **d** is the first one to have a minimum at grazing incidence and zero altitude. One-half of the locus of discrete minima, as β varies from 0 to $\tan^{-1}(2 \tan c)$, is shown by curve **m**. Line **e** shows the type of curve when β lies within the limits $\tan^{-1}(2 \tan c)$ and $2c$. At the points of intersection of the constant-β curves with the locus **t** the tangents to the former are perpendicular to the η_1 coördinate axis. For, at these points $\cos\eta_1 = \cot c \tan\frac{1}{2}\beta$ so that the radical symbolized by R_2 on page 403 vanishes. Consequently, the expression for $\dfrac{dD}{d\eta_1}$ becomes infinite. The theoretical values of the most important quantities pertaining to figure 6 are collected in Table II.

TABLE II.

	β	γ_1	D_1	D_m discrete minima	η_1 for D_m	D_2	η_1 for D_2
a ;	9° 42′ 0″	90°	27° 25′ 27″	10° 48′ 33″	84° 31′ 0″	10° 50′ 53″	84° 33′ 23″
b ;	20 0 0	"	36 7 50	22 2 42	78 15 37	22 23 22	78 37 49
c ;	43 37 58	"	49 6 5	45 22 46	57 47 41	49 6 5	63 24 48
d ;	60 47 39	"	58 24 43	58 24 43	0 0 0	68 54 13	49 0 52
e ;	77 42 0	"	73 51 46			89 4 0	25 46 20

The discussion of the mathematical properties of the curves **m** and **t** has been deferred to this place because the relevancy of these loci might not have been evident before the presentation of figure 6. The parametric equations of the curve **m** are given by formulæ (27) and (28), namely,

$$\sin\tfrac{1}{2}D = \tfrac{1}{2}\cot c \sin\beta,$$
$$\cos\eta_1 \;\; = \tfrac{1}{2}\cot c \tan\beta.$$

Elimination of the parameter β leads to

$$\sin\tfrac{1}{2}D = \frac{\cos\eta_1}{\sqrt{1 + 4\tan^2 c \cos^2\eta_1}}. \tag{56}$$

In general, the rationalized equation of the curve **m** may be written

$$\tan^2\eta_1 - \cot^2\tfrac{1}{2}D + 4\tan^2 c = 0 \tag{57}$$

Now, $$\frac{dD}{d\eta_1} = \frac{-2\sin\eta_1}{(1 + 4\tan^2 c\cos^2\eta_1)\sqrt{\sin^2\eta_1 + 4\tan^2 c\cos^2\eta_1}}$$

hence, when η_1 equals 0 and $\frac{1}{2}\pi$, $\dfrac{dD}{d\eta_1}$ becomes 0 and -2 respectively. Thus, the locus of discrete minima of fig. 6 intersects the η_1 and D coördinate axes at angles of 116° 33′ 54″ and 90°, in the order named. Both angles are independent of c.

The equations of the curve **t** are given by formulæ (15) and (40), namely,

$$\sin \tfrac{1}{2}D = \cot c \sin \tfrac{1}{2}\beta,$$
$$\cos \eta_1 = \cot c \tan \tfrac{1}{2}\beta.$$

Elimination of the parameter β leads to

$$\sin \tfrac{1}{2}D = \frac{\cos \eta_1}{\sqrt{1 + \tan^2 c \cos^2 \eta_1}} \tag{58}$$

In general, the rationalized equation of the curve **t** may be written

$$\tan^2 \eta_1 - \cot^2 \tfrac{1}{2}D + \tan^2 c = 0 \tag{59}$$

Since $\dfrac{dD}{d\eta_1} = \dfrac{-2 \sin \eta_1}{(1 + \tan^2 c \cos^2 \eta_1) \sqrt{\sin^2 \eta_1 + \tan^2 c \cos^2 \eta_1}}$

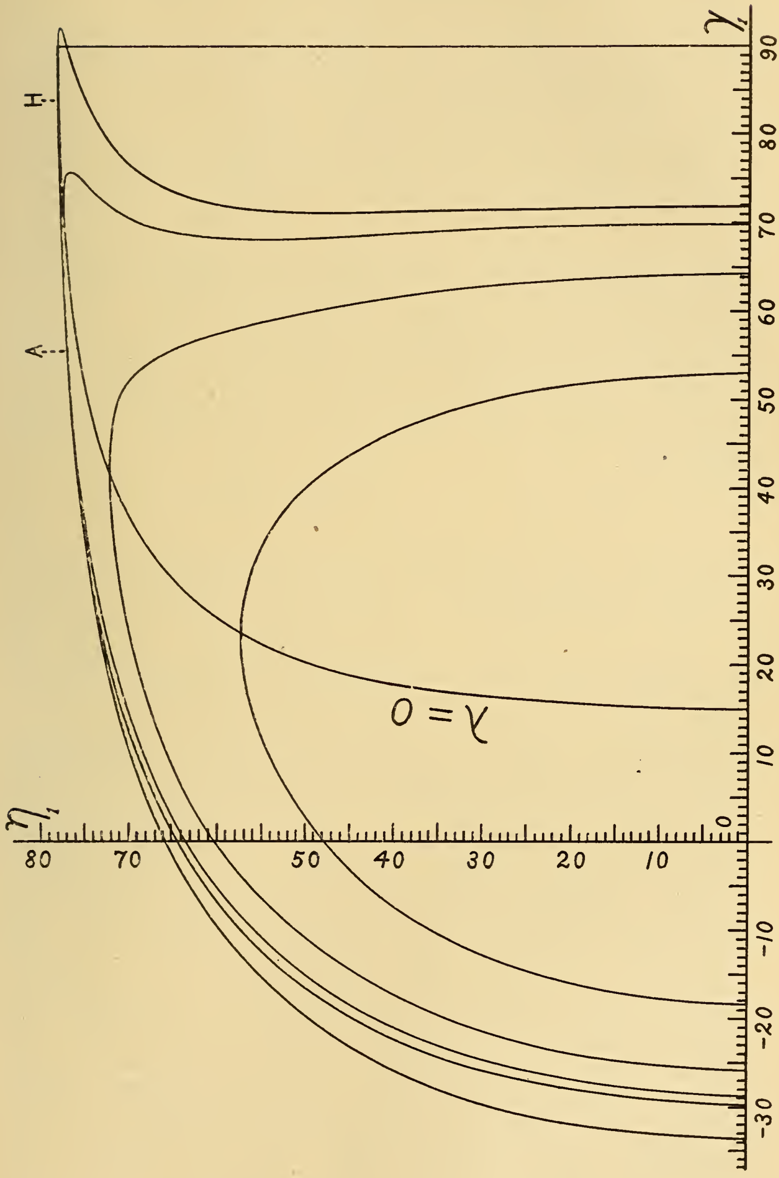
it follows that the locus **t** makes the same angles with the coördinate axes as the locus **m.** Therefore these curves have common tangents for $\eta_1 = \pm\frac{1}{2}\pi$. Although it can be shown analytically that the curves **m** and **t** have points of inflection for $D=0$, it is easier to obtain this result from inspection of the irrational equations of these loci, (56) and (58). The straight lines $D=0$, $\eta_1=\frac{1}{2}\pi$, and $\eta_1 = -\frac{1}{2}\pi$ are axes of symmetry.

Fig. 7 bears the same relation to the general $\gamma_1 \eta_1 D$ surface that figures 2, 3, 4, and 5 bear to the $\lambda \eta_1' D$ surface. As before, $n=1{\cdot}5$. In order to show the most complicated forms of the curves of constant deviation, and also to have negative values of the azimuth γ_1, ($\beta < c$), the comparatively small value 20° has been taken for the prism angle β. The values of D along four constant deviation loci, together with certain other theoretical data, are given in Table III.

TABLE III.

D	Intercepts, γ_1-axis.	Intercepts, η_1-axis.	Maxima and minima, $\lambda=0$.
14° 31′ 7″	+52° 49′ 12″ −18 18 5	±48° 2′ 12″	$\gamma_1=$ 23° 32′ 1″ $\eta_1=\pm$57 19 7
18 22 4.5	+64 11 30 −25 49 26	±60 18 1	$\gamma_1=$ 42 21 4 $\eta_1=\pm$72 38 47
21 0 0	+69 47 28 −28 47 28	±63 51 3	$\gamma_1=$ 70 16 32 $\eta_1=\pm$77 53 12
22 13 2	+72 1 49 −29 48 47	±64 46 2	$\gamma_1=$ 87 31 29 $\eta_1=\pm$78 37 9
Boundary	+90 0 0 −33 52 10	±65 59 16	$\gamma_1=$ 90 0 0 $\eta_1=\pm$78 37 49

FIG. 7.


γ_1
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
η_1
80
70
50
40
30
20
10
H
A
$\lambda = 0$

ϵ_0, D_1, and D_2 have already been given in Table I. The points A and H indicate the intersections of the curve for $D=22° \ 13' \ 2''$ with the left boundary locus. The abscissæ of these points are $\gamma_1=55° \ 48' \ 52''$ and $\gamma_1=84° \ 11' \ 8''$ respectively. The corresponding ordinates, which also pertain to the intersections with the right boundary locus, are $\eta_1=77° \ 30' \ 5''$ and $\eta_1=78° \ 35' \ 59''$, in the order named. This locus of constant deviation has been plotted beyond the right boundary. The equation of the locus of the algebraic maxima and minima of η_1, on the curves of constant deviation, has been designated as (44). This locus is marked "$\lambda=0$" in fig. 7. It crosses the γ_1-axis at the abscissa $\gamma_1=15° \ 5' \ 53''$. When the numerical value of the deviation is given, the coördinates of the points of intersection of the constant deviation locus with the curve $\lambda=0$ can be obtained from equations (30) and (31). As soon as η_1' has been evaluated, η_1 can be found at once by using (4). Then γ_1 may be obtained from (5) since, for $\lambda=0$, $\gamma_1'=\frac{1}{2}\beta$. In general, at the intersections of the left boundary locus with the axis of η_1

$$\frac{d\gamma_1}{d\eta_1} = \pm \sec c \cot \beta \sqrt{\sin (c+\beta) \sin (c-\beta)} \ ,$$

which requires $\beta \overline{\gtrless} c$, of course. For the special case of fig. 7 the acute angle obtained from the above derivative equals $64° \ 38' \ 8''$. The deviation at these points of intersection may be obtained from (42), and it equals $26° \ 59' \ 43''$. At the origin of coördinates of the $\gamma_1 \eta_1$ diagram the deviation is given by (43). For $\beta=20°$ and $n=1·5$ the deviation equals $10° \ 51' \ 57''$.

Returning to the loci of constant deviation, and inspecting fig. 7, it is seen that the curves which pertain to the smaller values of D only have algebraic maxima and minima of γ_1 for $\eta_1=0$, that is, in a principal plane. On the contrary, for relatively large deviations the curves have additional maxima and minima of γ_1. More specifically, each complete locus of large constant deviation has six stationary values of γ_1, namely, one maximum and one minimum on the γ_1-axis, two minima for numerically equal and finite ordinates, and two maxima for still greater (arithmetical) values of η_1. Stated in a slightly different manner, it is evident that a straight line parallel to the axis of ordinates, and lying wholly within one quadrant, may intersect a curve of constant deviation in one real point, or in two separate points, or in two coincident points and one other point, or in three discrete points, etc. The quantitative investigation of these points of intersection is equivalent to the discussion of the roots of the equation obtained by expressing η_1 as an explicit function of γ_1 and D. Rationalization of formula (35) leads to the following cubic in $\cos^2 \eta_1$, namely,

$$a_0 \cos^6 \eta_1 + a_2 \cos^4 \eta_1 + a_4 \cos^2 \eta_1 + a_6 = 0 \qquad (60)$$

where

$$a_0 = 16 \sin^4 c \sin^2 \beta \sin^2 \tfrac{1}{2} D \cos^2 \gamma_1 \cos^2 (\gamma_1 - \beta),$$
$$a_2 = 16 \sin^2 c \sin^2 \beta \sin^2 \tfrac{1}{2} D \cos \gamma_1 [\cos^2 c \sin \beta \sin (\gamma_1 - \beta) - \sin^2 c \sin^2 \tfrac{1}{2}D \cos \gamma_1 \cos^2 (\gamma_1 - \beta)] - [\cos^2 c \sin^2 \beta - 4 \sin^2 c \sin^2 \tfrac{1}{2} D + 4 \sin^2 c \cos \beta \sin^2 \tfrac{1}{2}D \sin \gamma_1 \sin (\gamma_1 - \beta)]^2,$$
$$a_4 = 8 \sin^2 c \sin^4 \tfrac{1}{2}D [2 \cos^2 c \sin^2 \beta \sin^2 (\gamma_1 - \beta) - \cos^2 c \sin^2 \beta + 4 \sin^2 c \sin^2 \tfrac{1}{2}D - 4 \sin^2 c \cos \beta \sin^2 \tfrac{1}{2}D \sin \gamma_1 \sin (\gamma_1 - \beta)],$$
$$a_6 = -16 \sin^4 c \sin^8 \tfrac{1}{2}D.$$

Obviously, equation (60) is altogether unmanageable. For this reason the conditions under which stationary values of γ_1 may arise will not be investigated. Suffice it to say that the constant deviation loci of fig. 7 are quite consistent with the above sextic in $\cos \eta_1$. There are several ways in which the cubic can give two and only two values of η_1 which pertain to the $\gamma_1 \eta_1$ diagram. One way is for the equation to have three real roots in $\cos^2 \eta_1$, two of which are positive and less than unity, while the third root is either negative or else positive but greater than unity. Another way is for equation (60) to degenerate. Thus for $\gamma_1 = \frac{1}{2}\pi$, $a_0 = 0$ and a biquadratic results. In order to test the correctness of the coefficients of the sextic, γ_1 was put equal to $\frac{1}{2}\pi$ and an attempt was made to factor the quartic which was obtained. The factors were found to be

$$(\cos^2 c - 4 \sin^2 c \sin^2 \tfrac{1}{2}D) \sin^2 \beta \cos^2 \eta_1 \mp \sin 2c \sin 2\beta \sin^2 \tfrac{1}{2}D \cos \eta_1 + 4 \sin^2 c \sin^4 \tfrac{1}{2}D = 0.$$

The quadratic with the upper sign is the equation which, when solved for $\cos \eta_1$, gives formula (26). [The sextic was also found to be satisfied by $\cos \eta_1 = \cot c \tan \beta$ when $\gamma_1 = 0$ and $\sin \frac{1}{2}D$ was taken from (42).]

Inspection of the constant deviation loci of fig. 7 throws some light on the most general form of intersection which a plane given by $\gamma_1 =$ *constant* can have with the $\gamma_1 \eta_1 D$ surface. [A discussion of equation (60), in this connection, is entirely out of the question.] In other words, a generalized constant-β curve of fig. 6, (for which $\gamma_1 = \frac{1}{2}\pi$), can have the following course. The deviation will have a minimum value for $\eta_1 = 0$, then as η_1 increases so also will D increase until a maximum value is reached. After this the deviation will decrease to a minimum and then increase up to, and beyond, the intersection with the boundary locus. The coördinates of some points of the $\eta_1 D$ curve corresponding to $\gamma_1 = 75°$ are given in Table IV. These points are not presented graphically because the deviation is roughly constant so that the wavy form of the curve would not be sufficiently marked on a small diagram.

[The possible bearing of the remarkably straight course of certain plane sections of the γ_1 η_1 D surface on the problem of diminishing the curvature of spectral lines has not been considered because it is not relevant to this paper.]

TABLE IV.

η_1	D	η_1	D
0° 0′ 0″	23° 59′ 28″	70° 43′ 52″	21° 45′ 1″
10 30 0	23 59 58	72 34 35	21 27 13
18 10 19	24 0 38	76 40 0	20 55 1
21 16 38	24 0 48	76 53 0	20 54 57
22 50 40	24 0 50	76 55 0	20 54 59
26 51 18	24 0 39	76 56 16	20 55 0
30 51 57	23 59 54	77 0 0	20 55 7
41 6 50	23 53 29	77 30 5	20 58 19
50 35 3	23 37 3	78 15 37	21 24 43
60 30 0	22 59 43	78 25 27	22 3 59

It may not be superfluous to follow the successive positions of the incident and emergent rays around the boundary loci in the actual case of a prism, that is, without reference to a sphere of projection such as is shown in fig. 1. The point of incidence will be considered fixed, so that the incident ray will generate a surface which consists of portions of a cone and of a plane, the incidence face of the prism. Commencing with grazing incidence in a principal plane, the emergent ray will also lie in the principal section and will have the azimuth $\gamma_2' = \sin^{-1}[n \sin(c-\beta)]$. This azimuth will be positive, zero, or negative, according as the angle of the prism is less than, or equal to, or greater than, the critical angle respectively. Keeping the incident ray in a grazing position and increasing the altitude of incidence, the emergent ray will have an azimuth which decreases algebraically, the altitudes of the incident and emergent rays being always equal. [See page 391.] At length, when the incidence altitude equals $\cos^{-1}[\cot c \tan \frac{1}{2}\beta]$ the emergent ray will begin to graze the second face of the prism. This is the position of simultaneous grazing incidence and emergence. Also, all of the positive half of the right boundary locus has been passed over. To continue farther, the incident ray must now leave the first face of the prism. As the azimuth of incidence decreases, the corresponding altitude must also decrease consistently with the equation

$$\eta_1 = \cos^{-1}\left\{\frac{\cot c \sin \beta}{\cos \beta + \sin \gamma_1}\right\}$$

While the incident ray is changing its position in the manner just indicated, the emergent ray will persist in a grazing position with ever decreasing altitude. Finally, when the azimuth of incidence attains the value $\sin^{-1}[n \sin(\beta - c)]$ both rays will again lie in the principal plane and the positive half of the left boundary locus will have been generated. This process may be continued for all possible negative altitudes until the entire boundary surface shall have been traced out. However, it is not necessary to consider negative altitudes in detail because a principal section constitutes a plane of symmetry. The preceding results are made concrete by the data in Table V, for which $\beta=20°$ and $n=1{\cdot}5$. Throughout this table the values of γ_2' correspond to grazing incidence, $\gamma_1 = 90°$. The left boundary values can be read off by reversing the ray; that is, by considering γ_2' as $-90°$ throughout and by changing the signs of the angles in the second column. The values thus obtained represent γ_1 when grazing emergence is maintained. Incidentally, the corresponding data for D and E are given.

TABLE V.

$\pm\eta_1$	γ_2'	D	E
0° 0′ 0″	33° 52′ 10″	36° 7′ 50″	36° 7′ 50″
6 0 22	33 43 26	36 4 12	36 16 34
16 37 53	32 43 30	35 39 43	37 16 30
26 0 43	30 56 39	34 57 51	39 3 21
35 52 50	27 53 17	33 50 53	42 6 43
46 39 12	22 29 43	32 6 0	47 30 17
57 0 45	13 43 50	29 45 11	56 16 10
65 59 16	0 0 0	26 59 43	70 0 0
72 38 31	−20 0 0	24 21 26	90 0 0
74 35 49	−30 0 0	23 28 46	100 0 0
76 1 0	−40 0 0	22 49 59	110 0 0
77 2 43	−50 0 0	22 23 22	120 0 0
76 46 27	−60 0 0	22 7 49	130 0 0
78 15 37	−70 0 0	22 2 42	140 0 0
78 32 21	−80 0 0	22 7 49	150 0 0
78 37 49	−90 0 0	22 23 22	160 0 0

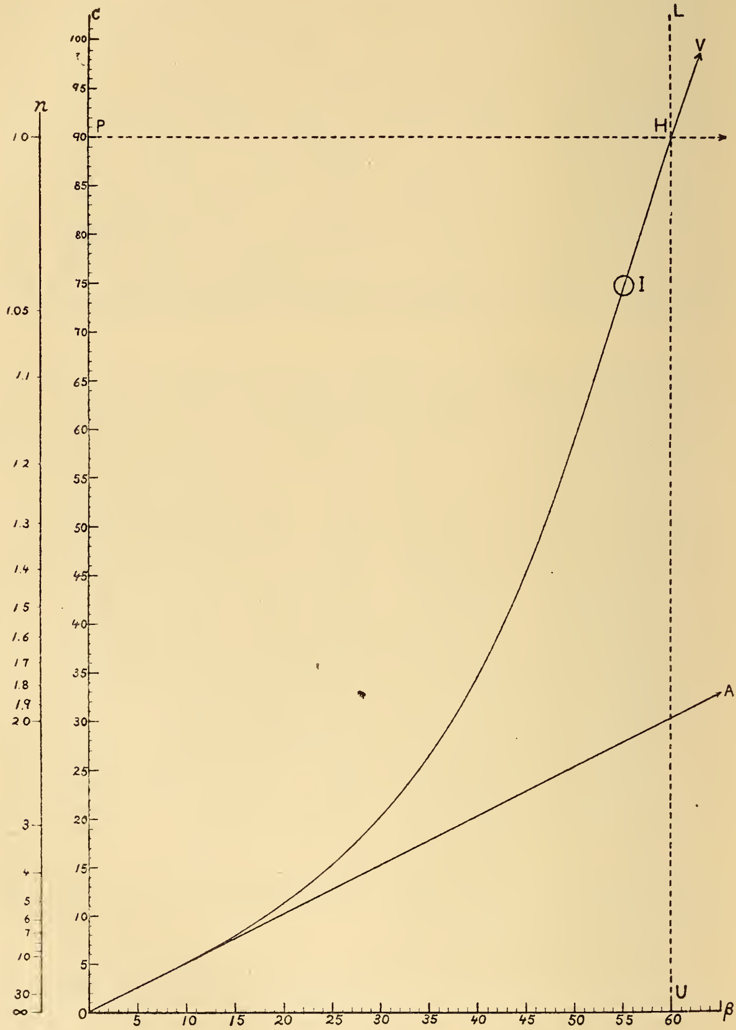
The properties of the lines which bound the domains characterized by the conditions

$$\beta = 2c, \ \cos\tfrac{3}{2}\beta = \cot c \sin\tfrac{1}{2}\beta, \quad \text{and} \quad \tan\beta = 2\tan c$$

will now be discussed. The most important portions of these lines are shown in fig. 8. Unlike the preceding diagrams, this figure is perfectly general, that is, it does not depend upon special values of the prism angle or of the index of refraction.

In order to plot quantities which are measured in terms of the same unit, the critical angle instead of the index of refraction is taken as ordinate with the prism angle as abscissa. For practical convenience a few arbitrary values of the index of refraction are indicated on the line parallel to the axis of ordinates. As the critical angle increases from 0 to $\frac{1}{2}\pi$ the index of refraction decreases from ∞ to 1. In order to avoid total reflection the condition $\beta \overset{=}{<} 2c$ must be fulfilled. Hence, for

Fig. 8.



transmission of light, the point characterizing the prism, (β, c), must lie within the angle AOP, since the equation of the straight line $\overline{OA}$ is $\beta - 2c = 0$. For points along this line only one ray can be transmitted and the small-circle arcs C′AC and C′BC of fig. 1 are tangent to each other. Again, by hypothesis, the relative index of refraction, n, must exceed unity, in other words, the critical angle must be less than $\frac{1}{2}\pi$. The equation of the straight line $\overline{PH}$ is $2c - \pi = 0$, hence, for transmission of plane waves, the characterizing point must fall inside the right triangle OQP, where Q denotes the point of intersection of the lines $\overline{OA}$ and $\overline{PH}$. The coördinates of Q are $\beta = \pi$ and $c = \frac{1}{2}\pi$.

It has been shown that the necessary and sufficient condition for equality between the deviations at grazing incidence in a principal plane and at simultaneous grazing incidence and emergence is

$$\cos \tfrac{3}{2}\beta - \cot c \sin \tfrac{1}{2}\beta = 0. \qquad \text{[See (49) and (50).]}$$

A portion of the curve representing this equation is shown as the line OV in fig. 8. [The reason for not plotting more of the curve OV is that the arc OIH alone has physical importance, and by drawing this arc on as large a scale as possible the practical value of the diagram is increased.] Hence, if the characterizing point (β, c) falls on this curve the relation $D_1 = D_2$ will hold. The straight line $\overline{UL}$ has the equation $3\beta - \pi = 0$, and it is seen that so much of the locus OV as lies within the domain of physical reality falls to the left of $\overline{UL}$. This shows very clearly the truth of the theorem that in order to have $D_1 = D_2$ it is necessary for the prism angle to have a value less than $\frac{1}{3}\pi$. The function

$$\cos \tfrac{3}{2}\beta - \cot c \sin \tfrac{1}{2}\beta$$

is positive on the left side of the partition OV and negative on the right. Therefore, the domain bounded by OIHPO contains the characterizing points of all prisms having the deviation at grazing incidence in a principal plane greater than the deviation at simultaneous grazing incidence and emergence. On the other hand, the region having the periphery OAQHIO includes all cases where $D_1 < D_2$. Since this area includes all points for which $\beta = \frac{1}{3}\pi$ it follows that the 60° prisms usually employed in spectroscopes always have $D_1 < D_2$.

The course of the curve OV will now be considered more in detail. In the first place

$$\frac{dc}{d\beta} = \frac{1 + 2\cos\beta - 2\cos^2\beta}{2(1 - 2\cos\beta + 2\cos^3\beta)}.$$

Hence, when $\beta = 0$, $\dfrac{dc}{d\beta} = \frac{1}{2}$, so that the line $\overline{OA}$ is tangent to the curve OV at the origin. At H, ($\beta = \frac{1}{3}\pi$), $\frac{dc}{d\beta} = 3$ and so the tangent to the curve makes an angle with the positive direction of the axis of abscissas equal to $\tan^{-1} 3 = 71° \, 33' \, 54''$. When $\beta = \cos^{-1} \frac{1}{2}(1 - \sqrt{3}) = 111° \, 28' \, 15''$, $\frac{dc}{d\beta} = 0$. It will be seen later that this stationary value pertains to a maximum of c. The curve OV passes through the point Q, which was defined as the intersection of the straight lines $\overline{OA}$ and $\overline{PH}$, since the coördinates $\beta = \pi$ and $c = \frac{1}{2}\pi$ satisfy equation (50). At this point $\frac{dc}{d\beta} = -1{\cdot}5$, and $\tan^{-1}(-1{\cdot}5) = 123° \; 41' \; 24''$. When the acute angle at H, the obtuse angle at Q, and the single stationary value of c between H and Q are taken into account, it becomes evident that the arc OIH is the only portion of the curve OV which lies within the triangle OQP, that is, within the domain of physical significance. Now

$$\frac{d^2c}{d\beta^2} = -\frac{(2 - 2\cos\beta - \cos^2\beta - 4\cos^3\beta + 2\cos^4\beta)\sin\beta}{(1 - 2\cos\beta + 2\cos^3\beta)^2},$$

hence for $\cos\beta = -\frac{1}{2}(\sqrt{3} - 1)$, $\frac{d^2c}{d\beta^2} = -\frac{1}{22}(5 + \sqrt{3})\sqrt[4]{108}$

so that the existence of the maximum mentioned above is established. At this point, c has the impossible value given by $\tan^{-1}\left[-\frac{1}{6}\sqrt[4]{12}(\sqrt{3} + 1)\right] = 139° \, 43' \, 9''$. The expression for $\frac{d^2c}{d\beta^2}$ vanishes for $\beta = 0$, $\beta = \cos^{-1}(0{\cdot}5709797)$, and $\beta = \pi$, thereby showing that there may be one point of inflection at the origin, another at $\beta = 55° \; 10' \; 53''$ with $c = 74° \; 48' \; 8''$ or $n = 1{\cdot}03624$, and a third at Q. That these points are truly inflectional is easily seen without proving that $\frac{d^3c}{d\beta^3}$ does not vanish. The second point of inflection lies at the center of the circle marked "1" in fig. 8. At this point the locus OV makes an angle of 72° 49′ 7″ with the axis of abscissas.

The equation

$$\tan\beta = 2\tan c$$

has been shown to be the necessary and sufficient condition that the discrete minima of deviation at grazing incidence or emergence shall coincide with their respective maximum, which occurs in a principal plane. [See (48).] Although the curve representing the above equation has not been plotted in figure 8, nevertheless, its course can be readily followed by the aid of the following data. In the first place

$$\frac{dc}{d\beta}=\frac{2}{1+3\cos^2\beta},$$

and

$$\frac{d^2c}{d\beta^2}=\frac{6\sin 2\beta}{(1+3\cos^2\beta)^2}.$$

The first derivative shows that maxima and minima cannot exist on the locus. At the origin $\frac{dc}{d\beta}=\frac{1}{2}$ and $\frac{d^2c}{d\beta^2}=0$, hence the curve has the line $\overline{OA}$ as the inflectional tangent at this point. For $\beta=60°$, $c=\frac{1}{2}\cos^{-1}\frac{1}{7}=40° \; 53' \; 36''$ or $n=\frac{1}{3}\sqrt{21}=1{\cdot}527525$, and $\frac{dc}{d\beta}=\frac{8}{7}$; $\tan^{-1}\frac{8}{7}=48° \; 48' \; 51''$. For $\beta=90°$, $c=90°$ or $n=1$, and $\frac{dc}{d\beta}=2$; $\tan^{-1}2=63° \; 26' \; 6''$. Also at this point $\frac{d^2c}{d\beta^2}$ vanishes and inflection takes place. For all points between the origin and the point $\beta=c=90°$ the locus is convex towards the axis of abscissas. Thus far the curve in question has properties like the line OV. Besides the origin, these two loci also intersect at the point $\beta=120°$, $c=\tan^{-1}(-\frac{1}{2}\sqrt{3})=139° \; 6' \; 24''$, which is to the right of the maximum on the locus OV. At this point $\frac{dc}{d\beta}=\frac{8}{7}$ and hence the tangent is parallel to the tangent at the point whose abscissa is 60°. For $\beta=180°$, $c=180°$, $\frac{dc}{d\beta}=\frac{1}{2}$, and $\frac{d^2c}{d\beta^2}=0$. Thus, there is an inflectional tangent at the last point which is parallel to the line $\overline{OA}$.

Let the point where the curve whose equation is $\tan\beta=2\tan c$ crosses the line $\overline{PH}$, of figure 8, be denoted by R. Then in the domain OAQRO there are no discrete minima at grazing incidence or emergence. In the region ORHPO there are two discrete minima, with one maximum in a principal plane, when $\gamma_1=90°$ or $\gamma_2'=-90°$. The last area is subdivided by the curve OV so that a still more detailed classification is possible. Since a segment of the line $\overline{UH}$ lies within the region ORHIO it is clear that 60° prisms can have discrete minima at grazing incidence, etc. However, for this to be the case, the critical angle must exceed $\frac{1}{2}\cos^{-1}\frac{1}{7}$ or the index of refraction must be less than $\frac{1}{3}\sqrt{21}$.

In conclusion, the author desires to thank Mr. Leigh Page for having verified the analytical work in this paper.

Sloane Physical Laboratory, Yale University,
New Haven, Conn., December, 1912.

Art. XXXV.—*The Shinarump Conglomerate;*[*] by H. E. Gregory.

Extent and Topographic Expression.

The conglomerate capping the Shinarump cliffs on the extreme northern border of Arizona is represented by exposures on the Navajo reservation and at other points south and east of the Colorado Canyon. It constitutes a stratum somewhat unusual in character and extent, and has accordingly attracted the attention of all geologists who have visited the Plateau Province. Howell,[†] who traced these beds more or less continuously from the Utah plateaus across Arizona and New Mexico, speaks of this stratum as "one hundred feet thick at St. George, forty or fifty feet to the east," and "coextensive with the Triassic of the Colorado Plateau." Gilbert[‡] remarks that "its persistence over large areas is . . . such as to excite wonder." Dutton expresses in even stronger terms what was apparently the belief of all field workers associated with Powell. In speaking of the Shinarump, including, however, not only the conglomerate but also the beds below, the following language is used:

> "Resting everywhere upon the Carboniferous of the Plateau country is a series of sandy shales, which in some respects are the most extraordinary group of strata in the West, and perhaps the most extraordinary in the world. . . . There are especially three characteristics, either one of which would render them in the highest degree conspicuous, curious, and entertaining.
>
> "First may be mentioned the constancy with which the component members of the series preserve their characters through the entire province. Wherever their proper horizon is exposed they are always disclosed, and the same well-known features are presented in southwestern Utah, in central Utah, around the junction of the Grand and the Green, in the San Rafael Swell, and at the base of the Uinta Mountains. As we pass from one of these localities to another, not a line seems to have disappeared, not a color to have deepened or paled. . . . The constancy is, so far as known to me, without a parallel in any formation in any other region."[§]

My own wanderings in the Plateau Province, dating from 1900, lead me to assent in general to the views expressed by the group of geologists who introduced the canyon land to the

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[*] Published by permission of the Director of the United States Geological Survey.

[†] Geological Surveys west of 100th Meridian, III, pp. 230–285.

[‡] Ibid. Pt. I, p. 175.

[§] Geology of the High Plateaus, p. 144.

FIG. 1.

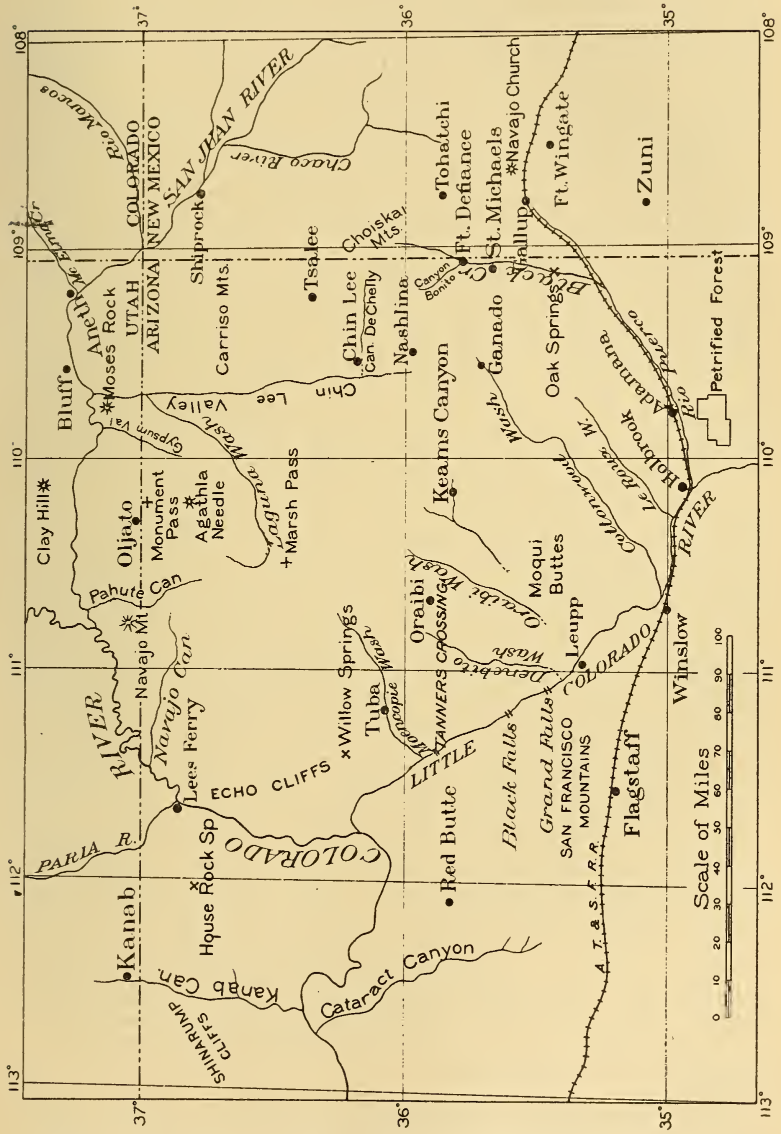

FIG. 1. Map of the southeast part of the Colorado Plateau Province.

scientific world; for although more detailed work justifies less sweeping statements than those used by Dutton, yet it is remarkable that a bed of such variability as a conglomerate and limited to a thickness of usually less than a hundred feet may be traced over such a wide area (see map, fig. 1). Where I have examined the Shinarump conglomerate, on the San Juan, at Oljato, Canyon de Chelly, Fort Defiance, Echo Cliffs, the petrified forest, and elsewhere, its uniformity in composition and texture, in stratigraphic position, and in relation to the beds above and below is striking; and even at Wingate and in parts of the Little Colorado valley where its typical characteristics are less in evidence, differences are less noticeable than likenesses.

Because of its siliceous character and its position between formations, which in general offer relatively little resistance to weathering, the Shinarump conglomerate assumes a topographic prominence apparently out of accord with its thickness. Wherever this bed attains its typical development it is a cliff or ridge-maker. To the north of the Colorado Canyon it forms the first step in the stairway which rises by giant treads from the Carboniferous platform to the summit of the High Plateaus. Where the strata are horizontal the Shinarump appears as a cap covering the beautifully banded Permian (Moencopie) beds. Where gently folded and exposed at the surface by the removal of the overlying shales, the conglomerate forms domes or cigar-shaped ridges as at Monument Pass and south of Toquerville. In places where folds have been eroded as at Fort Defiance, Oljato, and Bellevue, the conglomerate plays the rôle of a protecting cover of a group of beds which form well-defined cuestas. With steeper dip it becomes a ridge, as for example near the San Juan river, where the upturned edge of this stratum, dipping eastward at a high angle is cut for a distance of twenty miles into jagged pinnacles. The walls of the celebrated Canyon de Chelly and of Canyon Bonito are preserved by a mantle of Shinarump conglomerate, and its resistance to erosion is so much greater than that of the rock immediately beneath, that in several places the Shinarump projects as a molding which renders the cliff scalable only along weathered joints. West of St. Michaels, northeast of Agathla, and west of Willow Springs, as well as at points in Utah, the conglomerate forms a bare floor of grit many acres in extent; elsewhere it is strewn with debris from numerous landslides.

Structure and Composition.

As is to be expected from the nature of the rock, the Shinarump conglomerate varies in thickness and structural character. Powell remarks that "occasionally it is a little more than a coarse sandstone" with a maximum thickness of one hundred feet.* Dutton gives it a thickness of rarely over fifty feet, a conglomerate consisting of "fragments of silicified wood imbedded in a matrix of sand and gravel" and occurring in the midst of 550 to 750 feet of "transition shales."† The section at Toquerville, Utah, measured by Huntington,‡ shows fifty to sixty feet of hard conglomerate and sandstone. Newberry measured near Winslow, Arizona, a section containing twenty feet "of coarse, light brown sandstone, with white, bluish, red and black quartz pebbles varying in size from that of a pea to an egg," . . . "quite indistinguishable from the Carboniferous conglomerate of Ohio and Pennsylvania."§ Gilbert ‖ mentions thirty feet of gray conglomerate with silicified wood.

The writers quoted above speak of the Shinarump conglomerate as a single stratum, and at nearly all localities I have visited it appears as a distinct bed or set of beds maintaining its individuality throughout. It is terminated below by an unconformity, and continued above by shales containing beds of limestone conglomerates. While its thickness is usually less than one hundred feet, and occasionally less than twenty feet, yet at Moses Rock it (Oljato sandstone member = Shinarump conglomerate) forms a single massive bed 382 feet thick.¶

In contrast to the views expressed above, Ward** treats the Shinarump conglomerate as a group consisting of beds of diverse lithologic character. While recognizing clearly that the conglomerate so abundantly exposed in the Adamana fossil forest, near Winslow, at Red Butte, and on the Moencopie, is the true equivalent of the Shinarump conglomerate of Powell, Gilbert, and Dutton, and also that the conglomerate marks the upper limit of chocolate-brown, argillaceous shales charged with salt and gypsum, yet he considers this bed not as a single stratum but as a series consisting of "conglomerate and cross-bedded sandstone, often with pink and white striped, clay lenses, interstratified with gray argillaceous shales and variegated marls, the latter locally much thickened, forming brilliantly banded cliffs.†† For this series, 800 feet in thickness, Ward adopts the term "Shinarump conglomerate,"‡‡ changing it later§§ to "the Lithodendron member of his Shinarump for-

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* Geol. Surv. West of 100th Meridian, III, 283.

† Geology of the High Plateaus of Utah, p. 147.

‡ Bull. Geol. Soc. Amer., vol. xviii, p. 385, 1907.

§ Ives' Report upon the Colorado River of the West, 1857–58, Pt. III, p. 375.

‖ Geology of the Henry Mountains, p. 6.

¶ Woodruff, E. G.: Geology of the San Juan Oil Field, U. S. Geol. Survey Bull., No. 471, Pt. II, 1910, p. 183.

** Ward, L. F.: U. S. Geol. Surv., Monograph XLVIII, p. 19 ff. Ibid., p. 45.

†† Ibid., p. 45.

‡‡ This Journal, xii, pp. 201–13, 1901.

§§ U. S Geol. Surv., Monograph XLVIII, pp. 13–46.

mation, which is the equivalent of the Shinarump of Powell."

"Although perhaps the most prominent feature of this formation is the so-called conglomerate, which sometimes is in truth deserving of that name, and contains somewhat large but always well-worn pebbles and cobbles derived from underlying formations, it rarely happens that this aspect of the beds constitutes the major portion of them. In the first place, the conglomerate tends to shade off into coarse gravels and then into true sandstones. These sandstones are of a light color, contrasting strongly with the dark-brown sandstones of the Moencopie already described. They are, moreover, always more or less cross-bedded and usually exhibit lines of pebbles running through them in various directions. These are true sandstones, very hard, devoid of alumina, and scarcely affected by the winds, so that their angles are usually sharp and the ledges they form are abrupt and jagged. Although the sandstones proper generally occur lower down, there is no uniformity in this arrangement, and sandstones are often found in the middle and conglomerates more rarely at the top. But in addition to these the Lithodendron member embraces other classes of beds. There is a well-stratified layer of thinnish sandstone shales that is often seen immediately under the heavy sandstone cap. Some of these shales have a grayish color and are highly argillaceous. These layers tend to thicken even within the member itself, but especially farther out, and, what is more significant, they often become transformed into a bluish white marl. This condition can be seen between the beds of conglomerate in places where the Lithodendron beds are comparatively thin, as in the lower valley of the Little Colorado, where they are only about 300 feet in thickness. This feature is not very prominent, but at other places, as in the Petrified Forest region, where the Lithodendron beds attain their maximum thickness of 700 or 800 feet, this tendency on the part of certain beds to become transformed into marls is the most marked feature of the member. The marls here occupy much more than half of the beds. They are very varied in color, showing besides the white and blue tints a great variety of darker beds, such as pink, purple, and buff. These heavy marl beds, of which there may be several in the same cliff, are interstratified between conglomerates, coarse gravels, and cross-bedded sandstones, all of which taken together form the beautifully banded cliffs that are seen throughout the Petrified Forest, especially along its northern flank. It thus becomes necessary to include under one designation all of these varying beds, which often change the one into the other even at the same horizon within short distances."—(Ward, U. S. Geol. Surv., Mon. XLVIII, pp. 20–21.

It is evident that the Lithodendron member of Ward and the original Shinarump conglomerate of Powell lack not only family but racial likeness. I fully agree with Cross* that such

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* Jour. Geol., xvi, pp. 111–112, 1908.

a correlation "is a procedure requiring clear justification by facts not to be found in Ward's paper." Unfortunately detailed measured sections are not published by Ward nor to be found in his field notebooks on file in the Survey office. A knowledge of the exact position, extent and character of beds other than the conglomerate in his "Lithodendron member" cannot therefore be obtained. That the Shinarump frequently becomes a sandstone traversed by lines of pebbles, and that small lenses of clay shale occur in the midst of the conglomerate at one or two localities and even immediately at the lower contact, are facts of field observation. This shale, however, wherever observed, is unlike that forming the beds below the conglomerate, but resembles in essential particulars the beds occurring anywhere from one foot to 500 feet above the Shinarump conglomerate and even in the midst of the formation containing limestone conglomerate (Dolores of Cross; Leroux, in part, of Ward). In any case the line used by Ward to divide his "Lithodendron member" from his "Leroux beds" is arbitrarily drawn, and it seems better to limit the Shinarump conglomerate to the siliceous stratum or strata immediately above the chocolate shales and sandstones (Moencopie).

It is to be remembered, however, that the exact localities studied by Ward have not been examined in detail by other observers. The following statement of Darton, however, bears on this point:

> "I found this conglomerate at the base of the 'Lithodendron formation,' well exposed five miles northeast of Winslow, associated with two beds of sandstone and containing a large amount of petrified wood. It was traced along the north side of the Little Colorado Valley to Holbrook and thence up the Rio Puerco to a point considerably beyond Adamana. I did not notice that the conglomerate occurs at various horizons, as stated by Ward, but made no careful observations in that connection."—(Bulletin 435, U. S. Geol. Surv., p. 40.)

The Shinarump conglomerate, wherever observed, is wholly siliceous and gray to white, rarely brown, in tone. It varies in texture from conglomerate with pebbles two inches or so in diameter to coarse sandstone; rarely to fine sandstone. The coarser phases are well exposed at Fort Defiance, where pebbles of red, black, and yellow quartz (rarely chert) are mingled with fragments of silicified wood. All the larger pebbles (1/4″ to 1″; occasionally 2″) except those of wood are well rounded, and the smaller wood particles exhibit the same character. The matrix is identical in composition with the embedded pebbles and cobbles. In places the rock consists of a solid mass of pebbles; elsewhere a large pebble is set in a cubic foot of sandstone. Frequently a line of pebbles is seen traversing the sandstone for a distance of several feet. In places the sandstone is loosely cemented; generally it is firm, and occasionally becomes a glistening, hard quartzite conglomerate. At Oak Springs, Arizona, the constituents are pebbles of black, white and red quartz and chalcedony, all well rounded and attaining a size of one-half inch to two inches. At Oljato subangular clay pellets two inches or less in diameter are embedded with white, dark red, greenish, and black quartz and chalcedony. Fragments of wood several inches to several feet in length are present at every locality visited. Frequently the wood is present as logs; rarely it occurs as charcoal. At Oljato some chips are impregnated with copper; and at Leeds, Dutton reports that horn silver occurs in the wood. The universal presence of fossil wood constitutes the unique feature of the Shinarump conglomerate, and attracted the interest of Indians long before the coming of the white man. To the Piutes, the broken fossil logs are weapons of Shinárav, the Wolf god, a sort of Hercules, and Shinárav Mukwánkunt, as pointed out by Powell, is the original native name of the Shinarump cliffs. Navajos and Hopis explain the presence of wood in a similar manner. It may be remarked, in passing, that fossil wood is not confined to the Shinarump conglomerate, but occurs at several horizons above. In fact two extensive accumulations of wood on the Navajo Reservation, not yet described, occur 200–400 feet above the conglomerate. So far no fossil wood has been definitely assigned to beds below the Shinarump conglomerate. Wherever observed the Shinarump conglomerate is lenticular, cross-bedded, often excessively so, and variations in structure and texture both vertical and horizontal are characteristic.

The descriptions of the Shinarump conglomerate by Ives, Marcou, Newberry, Simpson, Powell, Dutton, Howell, Marvine, Ward, and other observers in the Plateau Province differ in no essential from that given above, and leave no doubt that all are speaking of the same stratum.

Origin of the Conglomerate.

A discussion of the conditions affecting the deposition of the Shinarump conglomerate is reserved for another time, since it seems desirable to limit the present paper to stratigraphic considerations. Suffice it to say that the conglomerate is subaërial in origin, was influenced in deposition by fluctuating climatic control, and that the source of the constituent pebbles has not been satisfactorily determined.

Stratigraphic Position.

The Shinarump conglomerate, together with the shales below, was originally assigned by Powell to the lower Triassic.

> "This escarpment is capped by a firmly cemented conglomerate containing many fragments of silicified wood, and over its surface are scattered many like fragments, and sometimes huge tree trunks, which are the remnants of rock at one time overlying the conglomerate, but now carried away by erosion. Underlying this cap are variegated sandstones and marls. The whole group is probably of lower Triassic age."*

Walcott (1879) placed the Shinarump conglomerate definitely at the base of the Triassic overlying the Permian, a determination used by Dutton in his Grand Canyon and Zuni reports. Since the publication of Dutton's classics, the stratigraphy of the region containing these beds has been studied by Ward (1900–01), by Woodruff (1910), and by the writer (1909–11). Important data, chiefly geographical, but also of indirect stratigraphic value, especially for the region north of the Canyon, was obtained by Davis,† by Johnson,‡ and by Huntington and Goldthwait.§

Ward concluded that not only the Shinarump conglomerate, but a large part (at least 700 feet) of the underlying shales (Moencopie) are of Triassic age. "Certain geologists hold that the series of beds which I have included under the name of Moencopie belong to a different system [from Shinarump] and is in some way connected with the underlying Paleozoic rocks. This view . . . is, in my opinion, quite untenable."‖ This grouping of part of the Moencopie with the Shinarump conglomerate and ascribing them both to the Triassic is an interpretation quite at variance with that expressed by other workers in these fields, unless the descriptions of Newberry, Marcou and Blake may be so interpreted. The chief difficulty arises from the fact that with the exception of a few indeterminate bone fragments found by the writer at Oljato no fossils have been collected from the Shinarump conglomerate. Its age is, therefore, to be determined by a study of its relations to the subjacent and superjacent beds, whose position in the time scale is fairly well known. The evidence thus derived is reasonably satisfactory and the conclusions drawn may, for the sake of clearness in presentation, be stated at this point: The Shinarump conglomerate marks the base of the Triassic of the Plateau Province. It is separated from the underlying shales

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* This Journal, vol. v, pp. 457–458, 1873.

† Excursion to the Grand Canyon of the Colorado, Bull. Mus. Comp. Zool., Harv. Coll., xxxviii, No. 5, 1901; Excursion to the Plateau Province of Utah and Arizona, ibid., xlii, 1903.

‡ Proc. Boston Nat. Hist. Soc., xxxiv, 1909, pp. 135–161.

§ Hurricane Fault in Toquerville District Utah, Bull. Mus. Comp. Zool., xlii, 1904, Geol. Ser. vi, No. 5.

‖ U. S. Geol. Sur., Monograph XLVIII, p. 22.

and sandstones of Permian age by a widespread unconformity. Above the Shinarump conglomerate lie in apparent conformity a series of calcareous and argillaceous shales with some sandstone and a group of unique limestone conglomerates, all deposited in upper Triassic time.

The setting of the Shinarump conglomerate in adjacent strata is indicated by the following portions of selected sections, which it will be noted were measured at widely separated localities.

Toquerville (*Huntington*)
(Bull. Geol. Soc. Am., xviii, p. 385, 1907)

Soft purple and red shales
Nodular gray shales
Hard Shinarump conglomerate and sandstone
Slight unconformity
Chocolate shale and sandstone, 150′–200′

Kanab Valley (*Walcott*)
(quoted by Cross, Jour. Geol., xvi, p. 106, 1908)

Gray conglomerate and sandstone; conglomerate formed of small, agatized pebbles and holding silicified wood 50′
Unconformity
Dark, reddish-brown, shaly sandstones, passing into a massive evenly bedded sandstone twenty feet from the summit of the bed. Ripple marks and mud cracks in upper part 135′

West Fork, Paria Creek (*Gilbert*)
(Geol. Surv. West of 100th meridian, iii, p. 160, 1875)

Variegated gypsiferous clays, with silicified wood 450′
White (to yellow) conglomerate, with silicified wood, resting on eroded surface of member below 0–75′
Unconformity
Chocolate gypsiferous clays; soft chocolate shale 225–300′

Tsalee (*Gregory*)

Shales and limestone of Dolores formation
Grey conglomerate and sandstone with with wood. Top of canyon wall 60′
Unconformity
Red, cross-bedded sandstone and shale 200′+

Chinlee (*Gregory*)

Argillaceous, calcareous, and arenaceous shales and limestones of Dolores formation 100′+
White sandstone and conglomerate with petrified wood 20′
Unconformity
Red sandstone forming canyon wall 100′+

Fort Defiance (*Gregory*)

Variegated shales and limestones 200′+
Limestone conglomerate 10′
Red, brown, purple shales 60′
Gray sandstone and conglomerate, hard, quartzose cross-bedded, pebbles of quartz, quartzite, fossil wood 20′
Unconformity
Sandstone and sandy shales, red, brown, pink, gray, breaks into ripple-marked slabs 300′+

Gilbert: Geology of Henry Mts., p. 6, 1880

Variegated clay shales, purple and white above, chocolate below, with silicified wood 300′
Gray conglomerate with silicified wood; the Shinarump conglomerate 30′
Unconformity
Chocolate-colored shale, in part sandy 400′

Last Bluff and southwest (*Howell*)

(Geog. Surv. West of 100th meridian, iii, pp. 271–272, 1875)

Variegated gypsiferous marls	400′
Shinarump conglomerate containing silicified wood	
Gray conglomerate with large quantities of petrified wood	50′
[Unconformity not noted]	
Chocolate, arenaceous and gypsiferous shales and marls.	

Gypsum Valley (*Woodruff*)

(Bull. 471, U. S. Geol. Surv., pp. 82–85, 1910)

Sandy variegated shales (Dolores)	1330′
Massive brown, gritty, cross-bedded sandstone (Oljato)	380′
Unconformity ?	

Red, sandy shale and massive, tan sandstones (Moencopie)	1260′

Oljato (*Gregory*)

Shales and limestone of Dolores formation	
Gray grit to conglomerate, quartz pebbles and fossil wood.	35′
Unconformity	
Argillaceous gray shales	3′
Chocolate-red, thin sandy shales	35′

Nashlina (*Gregory*)

Variegated and shales with limestone conglomerate	100′ +
Gray grits and conglomerate and wood	40′
Unconformity	
Chocolate sandstone	100′ +

The conclusion stated above and illustrated by the sections given, rests on the following facts of field observation: (1) continuity, lithologic similarity and equivalent age of the beds below the Shinarump conglomerate, (2) equivalence of beds above that datum, and (3) the presence of a widely extended unconformity.

(1) As to the nature and relations of the strata above the Shinarump conglomerate, there is substantial agreement, although inconclusive evidence of unconformity above this bed was noted by Woodruff* on the San Juan River, Utah, and by the writer in the Black Creek valley, Arizona. Everywhere these beds are shales and marls with layers of limestone and varying amounts of sandstone prevailingly calcareous. The limestone, usually a conglomerate, possesses such individuality that lithologic equivalence might be postulated on the evidence of this feature alone, and it is not surprising that this formation (Dolores of Cross; Leroux, in part, of Ward, "variegated shales" of other writers) should be described in terms which apply equally well to such widely separated areas as the La Plata mountains, Colorado, the Moencopie valley, Arizona, Leroux Wash, Arizona, and Fort Wingate, New Mexico In the course of my work in the Navajo country, opportunity has been afforded to trace these beds with inconsiderable interruptions from the Dolores River, Colorado, to Holbrook, Arizona, and from Echo Cliffs, Arizona, to Navajo Church, New Mexico, an experience which leaves no doubt in my mind that at all points the same formation is present.

* Woodruff: Geology of the San Juan Oil Field, U. S. Geol. Surv., Bulletin No. 471, Part II, p. 83, 1910.

Paleontological evidence indicating Upper Triassic age of the strata overlying the Shinarump conglomerate rests on fossils collected by Ward and Brown near Tanners Crossings,* described by Lucas;† by Gane at Clay Hill on the Lower San Juan,‡ fossils described by Lucas;§ by Walcott in the Kanab valley, fossils described by Eastman and Shimer;‖ by Woodruff in the San Juan Oil Field,¶ fossils identified by Stanton and Gilmore. Among other collections from these beds, and all exhibiting Triassic affinities, are bones and teeth found at several localities on the Navajo reservation during the field seasons 1909–1911. Fossils found at Oljato in the Shinarump conglomerate itself are too fragmentary for identification.

The list of fossils from the localities mentioned includes the following:

From Tanners Crossing, Arizona—*Heterodontosuchus ganei* Lucas, *Episcoposaurus* Cope, *Metoposaurus fraasi* Lucas, *Palæoctonus* Cope, *Placerias hesternus* Lucas; from Clay Hill, Utah—*Heterodontosuchus ganei* Lucas; from Kanab, Utah and Arizona—Vertebrates, *Pholidophorus*, several *Lepidotus*-like forms: Invertebrates, ammonitoid fragment, *Candona* (?) *Rogersii Jones*, *Estheria ovata* Lea; from San Juan Oil Field, Utah—*Unio cristonensis* Meek (?), *Viviparus* (?) sp., fragments of reptilian bone.

(2) The beds below the Shinarump conglomerate, while varying greatly in massiveness and relative proportions of shale and sandstone, have been recognized by all observers as equivalents throughout the extent of the Plateau Province. At nearly all localities where I have observed these beds they are shales and shaly sandstones of characteristic color, composition, and type of stratification, and the sections at Shinarump Cliffs, Utah, Little Colorado Valley, Arizona, Gypsum Creek, Utah, and Bonito Valley, Arizona, might be interchanged without detection so far as general features are concerned; but at other localities, especially Canyon de Chelly, the upper shales at least are replaced by massive, cross-bedded sandstone.** This change of character is fortunately not confusing so far as stratigraphic position is concerned, for the top of the

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* U. S. Geol. Surv., Monograph XLVIII, p. 15.

† Science, vol. xiv, p. 376, 1901; U. S. Nat. Mus., Proc., vol. xxvii, pp. 193–95, 1904.

‡ Cross, Jour. Geol., vol. xvi, p. 116, 1908.

§ This Journal, vol. vi, pp. 399–400, 1898.

‖ Cross, Jour. Geol., xvi, p. 107, 1908.

¶ Geology of the San Juan Oil Field, U. S. Geol. Surv., Bulletin No. 471, pt. ii, p. 85, 1910.

** Dutton: Zuni Plateau, p. 136–7; and Barton, Bulletin 435, U. S. Geol. Surv., plate IV, are in error in assuming that the massive walls and commanding towers of Canyon de Chelly and Canyon del Muerto are cut in Wingate (Triassic ? or Jurassic) sandstone.

Permian (Moencopie) is marked at this locality by an unconformity, immediately above which the Shinarump conglomerate occurs with all its distinguishing features.

The shales and sandstones below the Shinarump conglomerate are assigned to the Permian chiefly on the basis of collections of Walcott[*] in the Kanab valley, Utah. At this locality fossils were obtained from impure limestones and arenaceous shales in the midst of a series 854 feet in thickness, terminated above by the unconformity marking the base of the Shinarump conglomerate, and below by the upper limestone of the Aubrey group (Kaibab limestone of Darton). Twenty-three genera represented by thirty-four species and including *Pentacrinus*, *Mytilus*, *Pleurophorus*, *Schizodus*, *Bakewellia*, *Pteria*, *Lingula mytiloides*, *Discina nitida*, *Rhynchonella Uta*, were found to occur in the upper portion of the strata. The lower chocolate-colored limestone furnished specimens of *Myalina*, *Schizodus*, *Nucula*, *Aviculopecten*, *Murchisonia*, *Naticopsis* and *Goniatites*. While fossils at numerous other localities where the Permian is exposed are much to be desired, yet the unmistakable evidence from Kanab taken in connection with lithologic similarity and the unconformable position of these beds below the Shinarump conglomerate, furnishes fairly satisfactory determinations of age relationship.

(3) The unconformity between the Permian (Moencopie) and the Shinarump conglomerate has been recognized repeatedly. Gilbert states:[†]

> "The Shinarump conglomerate, although remarkably persistent for a conglomerate, thins out and disappears at a number of points, and at the margins of its areas it is evident to the eye that it occupies depressions of the surface on which it rests."

Dutton remarks:[‡]

> "In the Permian, Trias, and Jura we find instances of those peculiar unconformities by erosion without any unconformity of dip in the beds. Perhaps the most widely spread occurrence of this kind is the contact of the summit of the Permian with the Shinarump conglomerate which forms the base of the Trias. Wherever this horizon is exposed this unconformity is generally manifest."

Huntington[§] notes the unconformity in a measured section at Toquerville; Walcott describes and figures the unconformity between Paria and House Rock Springs, Utah,[‖] where a

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[*] This Journal, vol. xx, pp. 221–25, 1880.
[†] Geology of the Henry Mountains, p. 8.
[‡] U. S. Geol. Surv., Monograph II, p. 211.
[§] Bull. Geol. Soc. Am., xviii, p. 383, 1907.
[‖] Ibid., i, pp. 63–64, 1890.

cliff of Permian shales buried by conglomerate indicates a long erosion interval. It is interesting to note that westward from House Rock Springs across the Kaibab fold, not only the upper sandstones of the Permian, but also the conglomerate is absent, thus bringing the Triassic shales in immediate contact with Permian shales, and removing those features which most clearly indicate an erosion interval. Davis* figures the unconformity at Yellowstone Springs, previously noted by Dutton,† and I have seen it at several localities including those already mentioned.

An unconformity below the Shinarump conglomerate was not reported by Ward nor by Darton along the line of the Santa Fe, and my rapid reconnaissance of parts of the same region led to no satisfactory results. Likewise no conclusive evidence of unconformity was obtained in the San Juan Oil Field either by Woodruff or by me. It may be that the unconformity does not exist on these borders of the Plateau Province; but it is also possible that its presence may have been overlooked. An unconformity without change of dip, especially in places where the conglomeratic phases are absent and where the rocks approach uniformity in color, may escape notice during the rapid traverses incident to reconnaissance. In any case the abrupt transition from the characteristic Permian beds to the unique series lying immediately above indicates a marked change in physical conditions, and even in the absence of direct proof the existence of an unconformity might be postulated.

In this connection I must dissent from any general acceptance of the statement of Ward that the Shinarump conglomerate "contains somewhat large but always well-worn pebbles and cobbles derived from the underlying formations."* At no place in Utah, Arizona, or New Mexico, have I observed in the Moencopie material from which the quartz pebbles of the Shinarump conglomerate may have been derived. In fact, the origin of such quantities of siliceous material at this horizon is so far an unsolved problem.

Correlation.

The relation of the Shinarump conglomerate to the Triassic strata of southwestern Colorado has been discussed by Cross,‡ whose detailed studies of the mountains of southern Colorado have furnished a series of stratigraphic units which have greatly facilitated field work in the Navajo country. The equivalents of the La Plata, McElmo, and Dolores formations of Colorado

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* Bull. Mus. Comp. Zool., Harv. Coll., vol. xlii, p. 15, fig. 5.
† U. S. Geol. Surv., Monograph II, pp. 44–80.
‡ Jour. Geol., vol. xvi, 1908.

are widely exposed in southern Utah, northeastern Arizona, and northwestern New Mexico. The typical Shinarump conglomerate, however, does not appear in the sections so far published for the San Juan country. In discussing its absence Cross* suggested that the Shinarump conglomerate may be represented in Colorado by the "Saurian conglomerate" found in the midst of the Dolores (Leroux, in part, of Ward) (Triassic) formation,—a view which has served the useful purpose of a working hypothesis.

The "Saurian conglomerate," a rock consisting typically of elongated pebbles of limestone frequently accompanied by chert (the "mortar beds" of Ward), occurs at each of the many localities where the Dolores is exposed. Several beds are present, usually grouped in the middle or lower half of this formation. Identity of position, composition, structure, and fossil content, leave little room for doubt that these limestones extend from the La Plata mountains to the Little Colorado, and from Lee's Ferry to Fort Wingate. Wherever observed, the "Saurian conglomerate" occurs in the midst of variegated shales and is above, sometimes several hundred feet above, the Shinarump conglomerate.

The evidence so far collected from the entire area under discussion has led to complete agreement on the part of Cross † and the writer, that the Shinarump conglomerate is not represented in the Dolores of southwestern Colorado, and that the "Saurian conglomerate" layers of the Dolores lie above the Shinarump in the San Juan valley. The Shinarump may not have extended beyond the Plateau Province, but may have been removed during the pre-Dolores erosion interval, demonstrated by Cross, the extent and significance of which for the Plateau Province I propose to discuss in another connection.

The stratigraphic location of the Shinarump conglomerate involves the position, extent, and age of the underlying shales and sandstone (Moencopie of Ward). In regard to these beds some confusion exists in the literature because no attempt was made by Ward to harmonize his studies with the results obtained by Powell, Dutton, Gilbert, and Walcott, and because the preliminary conclusions of Cross‡ were substantially modified as the result of later study.§

My observations on this point are in accord with the results of Ward's study; that upwards of 700 feet of chocolate shales and sandstone (Moencopie) rest unconformably upon the "Upper Aubrey" (Kaibab limestone of Darton) Carboniferous, and are

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* Idem, pp. 121–122.

† Private communication, February 10, 1913.

‡ Bull. Geol. Soc. Amer., vol. vi, p. 482, 1905.

§ Jour. Geol., vol. xvi, p. 111, 1908.

capped by the Shinarump conglomerate. However, as regards the vertical extent of the Permian beds, I am unable to assent to the conclusion of Ward, who considered it "very probable that the lower portion of the Moencopie beds belongs to the Permian."* In the absence of evidence to the contrary, it appears to me better to assign all strata between the "Upper Aubrey" (Kaibab limestone) and the Shinarump conglomerate to the Permian. This conclusion is in harmony with Walcott's studies and with the views of Cross and coincides with the results obtained by tracing of outcrops southeastward from the mouth of the Little Colorado.

In the discussion of the stratigraphy in the San Juan Oil Field,† the Oljato sandstone member is ascribed, with considerable hesitation, by Woodruff, to the Permian. This was done after a conference with the present writer, and quite with my approval. While we both recognize the distinctive character of this bed, yet it seemed "out of place," and on the whole it was thought best to treat it as the upper member of the sandstones which form such a prominent part of the lower "Red Beds" along the San Juan. Massive tan sandstones underlie the Oljato and the evidence of unconformity is not at all clear. Later field studies have led me to the belief that the Oljato sandstone member may be wholly or in part the Shinarump conglomerate,—an interpretation which does not conflict with the field evidence and is entirely in agreement with the interpretation of the stratigraphy of the Plateau country as a whole.

Conclusion.

The extension of field work over the previously unexplored area between the San Juan River and the Santa Fe railroad and east of the Little Colorado River reveals the fact that the Shinarump conglomerate of Powell is practically coextensive with the province; that it occupies the base of the Triassic and serves as a datum plane for stratigraphic work in this area; that the strata below are Permian, and that the strata above are Upper Triassic; that the conglomerate itself is Triassic, but whether Upper Triassic or older is undetermined.

Yale University.

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* U. S. Geol. Surv., Monograph XLVIII, p. 19.

† U. S. Geol. Surv., Bulletin 471, Pt. II, p. 83, 1910.

ART. XXXVI.—*A Danger to be Guarded Against in Making Mineral Separations by Means of Heavy Solutions;* by W. F. HILLEBRAND.

THAT one or another of the heavy liquids and solutions used for making mineral separations acts chemically on a few minerals has long been known. Thus, the solution of potassium and mercuric iodides, known as Sonstadt's or Thoulet's solution, attacks metals and probably certain oxides and sulphides. Rohrbach's solution of barium and mercuric iodides probably has similar action. Klein's solution of cadmium-boro-tungstate decomposes carbonates as well as attacks metals. Doubtless others have their specific effects.

So far as known, the actions hitherto observed have resulted beyond doubt in complete solution or profound disruption of the mineral subject to attack, but such action, being easily noticed, involves no serious risk. I have now to record an instance in which the attack involves a chemical interchange between heavy solution and mineral without producing any alteration in the latter, that is visible to the eye.

There was sent me for examination, some two years ago, by the Foote Mineral Company, of Philadelphia, a canary-yellow crystallized mineral from Paradox Valley, Montrose County, Colorado, which was supposed to be carnotite, this being essentially hydrous potassium-uranium vanadate. This mineral proved to be very similar to carnotite in composition, but with calcium replacing potassium. Later, the attempt was made to purify some of it by the potassium-mercuric iodide solution, but analysis then gave for it the composition of carnotite. Suspecting the reason, another specimen was divided into two portions, one of which was analyzed in its original state, the other after action upon it of the heavy solution for 18 hours and complete removal of the mercury salt. This was found to have lost most of its calcium and to have taken up the exact equivalent of potassium. The composition of the two portions with respect to the major constituents is shown below, a number of minor elements being disregarded, also the quartzy gangue.

It should be remarked that the material analyzed in this case was a mixture, the copper belonging in great part if not altogether to a greenish vanadate, to which probably a portion of the calcium also belongs.

The only essential change in the composition of the mineral appears to be with respect to the calcium and water. The molecular ratio of $CaO+K_2O$ in the two portions is 954 to 952, indicating exactly equivalent replacement of calcium by potas-

	Mineral untreated. Per cent	Mineral treated by Thoulet solution. Per cent
V_2O_5	18·03	18·31
UO_3	53·71	55·37
CaO	5·20	1·72
K_2O	·24	6·08
CuO	4·16	4·22
SiO_2, P_2O_5, BaO, Al_2O_3, MgO, Na_2O	2·45	1·91
H_2O and loss	16·21	12·39
	100·00	100·00

sium. The decrease in the water content of the treated portion practically accounts for the somewhat higher values for vanadium and uranium in it. The difference in the water values may, however, not be real, since it is now known that the water content of the mineral may vary several per cent, according as the weather is dry or humid. Striking is the fact that the copper does not seem to have been affected by the heavy solution. Whether complete replacement of the calcium would have resulted from longer treatment has not been determined by reason of lack of material and opportunity. It was noted in earlier tests of treated specimens that the calcium had not been wholly displaced. This is in agreement with the observation that the copper vanadate probably carries calcium, and, since the copper of that mineral has not suffered removal, it is not improbable that whatever other bases it may carry were also retained.

The yellow calcium mineral, when treated with Thoulet solution, showed, according to Mr. H. E. Merwin, a decrease in the optic axial angle of 25° as compared with untreated material of approximately the same state of hydration.

The observation detailed above shows how important it is in the use of heavy solutions to assure oneself that chemical changes of the kind shown are not incurred. Question naturally arises as to the validity of the compositions that have been assigned to one and another mineral which has been separated from others by heavy solutions before analysis.

The calcium carnotite experimented with is probably identical with the *tuyamunite* of Nenadkevich* and will form the basis for detailed description by Mr. Merwin and myself in a later paper.

Bureau of Standards,
Washington, D. C., Feb.

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* Bull. Acad. Sci. St. Petersburg, 1912, p. 945.

Art. XXXVII.—*Two Varieties of Calciovolborthite (?) from Eastern Utah;* by W. F. Hillebrand and H. E. Merwin.

About nine or ten years ago Mr. J. M. Boutwell brought to the United States Geological Survey specimens of minerals from a mining prospect near Richardson, in the canyon of Grand River, Southeastern Utah. One of these, yellow-green in color, was found to be, on the basis of quantitative tests by one of us (H.) in the Survey laboratory, a hydrous vanadate of copper; the other, greenish yellow, a hydrous arseno-vanadate of copper and calcium. These minerals have been referred to in print* by Mr. Boutwell, but the analyses were not published, since it was expected that more material would become available for study. This hope was not realized and most of the specimens were later destroyed by fire.

Soon after first sight of the minerals one of us (H.) saw, in the Utah exhibit at the World's Fair in St. Louis in 1904, splendid specimens of what seemed to be one or both of these minerals, but nothing definite could be learned as to their source, nor is it known what became of them.

A "green encrusting mineral" called volborthite is mentioned in the Quarterly of the Colorado School of Mines (vol. iii, No. 3, 1909) as having been found in a mining prospect, now abandoned, at or near Garos (Garo ?) in Park County, Colorado, and it was said that fine specimens were exhibited at the World's Fair in St. Louis. From the imperfect description it would seem as if this might be related to or identical with one of the minerals from Utah.

Within the past two years we have received from the Foote Mineral Co. of Philadelphia, a mineral on sandstone from Paradox Valley, Montrose County, Colorado, which is beyond doubt identical with one of Mr. Boutwell's minerals, as revealed by recent comparison with the microscope.

It seems then timely to put on record our present knowledge of the minerals, although the analyses made long ago by one of us (H.) lead to no clearly-defined formulas. It is to be remembered that only Mr. Boutwell's material has been analyzed. In the case of the yellow green mineral the analyses had to be made on as little as 0·2, 0·16, and 0·13 grams, respectively, of the scrapings and pickings from the sandstone on which it occurred. For the greenish yellow mineral two half-gram portions were available, each yielding about 0·4 gram of soluble components. But for neither mineral was the soluble matter solely the mineral under study. Small amounts of carbonates and perhaps silicate of copper were included

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* U. S. Geol. Survey, Bulletin 260, pp. 205–206.

besides ferric and other oxides, foreign to the vanadates, but complicating the analysis and interfering with deductions.

Both minerals occur, sometimes on the same hand specimen, in rosettes and patches of minute reticulated scales on surfaces of sandstone, often intimately associated with thin coatings and stains of other copper minerals—carbonates and possibly chrysocolla—which made it impossible to secure material of great purity for analysis. Mr. Boutwell mentions occasional "carnotite and small yellow crystals, slightly darker than this carnotite," as being "intimately associated with the green crystals," but we have observed neither of these on the specimens now available. The rosette forms spoken of are often distributed singly, but more often grouped and intermingled, presenting then a very handsome appearance, especially in the case of the yellow green mineral.

1. *Yellow-Green Variety.*—Rosettes and patches of reticulated scales. The aggregates have a dark yellow-green color (YG), Shade 1, of the Bradley Color Scale.* In powder and in scales under the microscope the color is brilliant green yellow (GY). But few data as to crystalline form could be obtained from the material from Paradox Valley, Colorado, but that from Richardson, Utah, furnished a few triangular, hexagonal and elongated scales, which, within the limits of error (3°), possessed hexagonal symmetry. However, the mineral is not hexagonal, but probably monoclinic, as the optical study showed. On account of the aggregated character of the material nothing definite can be said concerning the hardness and cleavage of the mineral, although the thinnest scales appear to be cleavage fragments. Lack of material of sufficient purity prevented the determination of the specific gravity.

An optic axis and the bisectrix γ emerge at angles of about 50° in air on opposite sides of the normal to the plane of the scales. The optic axis is strongly dispersed, with the red fringe of the hyperbola on the convex side. Measurements of the optical axial angle, 2V, gave the following average results from values that varied 5° for different sections: in Li-light 68°, Na-light 83°, Tl-light 89°. The mineral is, therefore, optically positive for red and negative for violet. The measurements indicate that the bisectrices are dispersed. Determination of the extinction position of plates for light of different colors established the essential coincidence of the optic planes for all colors, although most sections do not extinguish completely in white light. The dispersion is, then, inclined, and the mineral is probably monoclinic. The indices of refraction, α and β, for Na-light, measured by immersion in highly refracting liquids, are 2·01 and 2·05. γ calculated = 2·10.

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* This scale can be found in Mulliken's Identification of Pure Organic Compounds; Wiley & Sons, New York.

The extremely strong inclined dispersion is noteworthy. Between the optic axes for Li-light and Tl-light there are angles of 28° and 7°. The axis emerging in the field of the microscope is dispersed 7°. The bisectrices are dispersed 18°. The plane of the optic axes bisects the angle of the triangular plates. This relation and inclined dispersion are strong evidence of monoclinic symmetry. The absorption of light by the crystals was studied in a general way by observing them in light of different wave lengths. No sharp absorption bands were disclosed and there is little absorption in the bright part of the spectrum, but beyond 530μμ and 630μμ absorption in all three of the principal directions increases steadily and sensibly equally, except that beyond 470μμ differences are noticeable.

2. *Greenish Yellow Variety.*—The arsenical variety of the mineral has the same reticulate appearance as that just described. The color is dull green (G, shades 1 and 2), and is in some cases only a thin film covering crystals of the yellow-green mineral. This fact was not known when the analyses were made, hence it is possible that the composition found represents a mixture. Under the microscope the green crusts are seen to be very minute, doubly refracting crystals of refractive index about 1·92. They absorb at the ends of the spectrum, noticeably beyond 500μμ and 660μμ. This mineral is pseudomorphic after the yellow-green variety.

	Yellow-Green		Green-Yellow	
	Percentages	Mol. Ratio	Percentages	Mol. Ratio
V_2O_5	30·6*	175	16·0*	168
As_2O_5	1·1		17·2*	
P_2O_5	·3		·8	
CuO	48·4*	713	37·1*	769
CaO	3·9*		15·3	
BaO	2·7		2·3	
MgO	·3		·5	
K_2O / Na_2O	·7		·2	
H_2O, 105° —	1·8	100	1·0	55
H_2O, 105° +	6·4	355	4·3	239
CO_2	2·4	60	·9	32
SiO_2	·6		·7	
Fe_2O_3	·8		·5	
Mn_3O_4, Co_3O_4, Al_2O_3 †	-------		3·2	
	100·0		100·0	

*Mean of two closely agreeing results.

† As weighed after precipitation together. Original condition unknown.

Analyses and Discussion.—In calculating the analytical results shown on the preceding page there was deducted 30·6 per cent of matter insoluble in very dilute nitric acid in the case of the yellow-green mineral, and 13·5 per cent in the other, and calculating to 100. The original analytical summations were 99·5 and 101 respectively.

If CO_2 and SiO_2 are allowed for as normal carbonates and metasilicates, an assumption not entirely in accord with the facts, but the best that can be made, the molecular ratios become:

	V_2O_5	:	RO	:	H_2O total	:	H_2O, below 105°
Yellow-green	1		3·73		2·6		2·03
Green-yellow	1		4·37		1·75		1·42

In view of the character of the material analyzed and the doubt expressed a little above as to the homogeneity of one of the samples, the above ratios do not permit us to decide that the two minerals should receive different formulas. The difference is most marked in the water, but under the circumstances this should not force a decision, especially since we know nothing, in the first place, as to the function of the water—whether truly water of crystallization or in its amount a function of atmospheric humidity and temperature—nor, in the second place, how much of it is to be assigned to contaminating minerals. Until better material and better analyses are available we prefer to regard the minerals as related to each other and of the same type formula, the green derived from the yellow by partial replacement of V_2O_5 by As_2O_5 and of CuO by CaO.

When it comes to establishing the relationship of these minerals to others already known, difficulty arises also. Unquestionably the nearest known relative is calciovolborthite, for which, on the basis of widely divergent analyses, Dana gives the formula $4(Cu,Ca)O.V_2O_5.H_2O$.

Optical data concerning calciovolborthite are entirely lacking. We do not feel justified in making new species out of the minerals herein described, but choose to refer them both for the present to calciovolborthite, assigning that name to the yellow-green variety and arsenical calciovolborthite to the greenish-yellow derivative.

The original belief of one of us (H.) as published by Mr. Boutwell, that the arsenical variety is a new species, distinct from the other, we do not care to press, although it may prove to be so.

As to the name calciovolborthite, it is difficult to see how it ever came to be applied originally by Rammelsberg,* since the

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* The name Kalk-volborthit was not used by Credner, the first describer of the mineral, as a statement in Dana's Mineralogy leads one to infer.

mineral called by it differs fundamentally from volborthotite, although the latter is also a copper vanadate. It is very unfortunate that a name so inappropriate and misleading should have been given.

In 1908 J. Antipoff* gave in Russian a very unsatisfactory description of a new occurrence of uranium and vanadium minerals at Tuya Muyun, a hill in the Alai Mountains, in the province of Ferghana, Russian Turkestan.

One of the minerals mentioned is regarded as allied to volborthite, and is called Turkestan volborthite, although it approaches calciovolborthite far more closely in composition, as the figures below show:

V_2O_5	41·03
MoO_3	·23
CuO	29·45
CaO	20·40
Fe_2O_3 Al_2O_3	2·80
SiO_2	1·10
H_2O	4·55
	99·56

The formula assigned by the author is

$$(VO_4)_4Cu_3Ca_3 . 2H_2O.$$

Later, in 1909, K. Nenadkevitch† described, as the predominating vanadium mineral at the same locality, another vanadate under the name turanite, and assigned to it the formula $5CuO . V_2O_5 . 2H_2O$. It is said to occur as compact or radiating, olive-green, spherical concretions and kidney-like crusts in cavities of malachite and ore-bearing limestone.

Bureau of Standards and Geophysical Laboratory of the Carnegie Institution,
Washington, D. C., Feb.

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[*] Gornii Journal, iv, 255–267, 1908. Through Neues Jahrb. für Min., etc., ii, p. 37, ref., 1909.

[†] Bull. Acad. Sci., St. Petersburg, 1909, 185–186.

Art. XXXVIII.—*Some Interesting Mineral Occurrences at Princeton, N. J.*; by Alfred C. Hawkins.

[Contributions from the Geological Department of Princeton University.]

Recent geological investigations undertaken by the writer in the vicinity of Princeton, N. J., have brought to light the presence of certain unusual mineral deposits there, for some time known to exist, but not, until now, studied in any detail. The mineral species afforded are interesting both in their geological and mineralogical associations and in their crystallographic development.

Fig. 1.

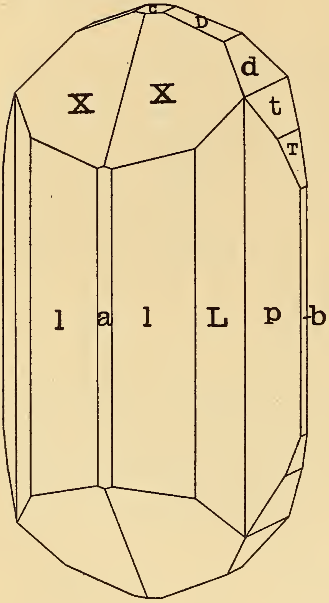

Fig. 2.

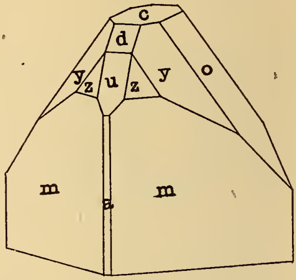

Fig. 3.

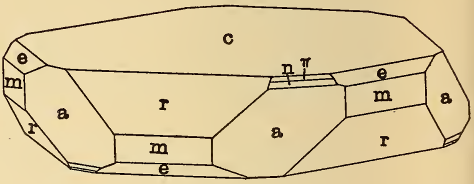

Fig. 1, Brookite. Fig. 2, Barite. Fig. 3, Ilmenite.

The rocks in the section of New Jesrey herein mentioned are the shales and sandstones, with associated diabase, belonging to the Triassic system. Quarries within the town of Princeton have recently exposed intensely brecciated areas of very limited extent, marking crushed zones in the dense sandstone layers. Within these breccias the mineral species here described occur, occupying the spaces between the angular grains of the crushed and shattered rock. The crystals obtained are small but often exceedingly brilliant and gem-like.

Geology.—There are three principal joint directions, the most important of which, occupied by the major joint series (tension joints), is remarkably constant in direction throughout the area. It widely affects the sedimentary rocks, and is also found on the borders of the intrusive diabase mass of Rocky Hill, an extension of the Palisade sill. Titanium minerals—brookite and ilmenite—are found in these joints, apparently far removed from diabase, together with analcite and barite, whose derivation from the intrusive rocks is indicated by the occurrence of the same minerals in similar joints in the immediate vicinity of the trap rocks at Byram, Hunterdon Co., N. J., and elsewhere. The occurrence of such minerals in the joint cavities of sedimentary rocks, two miles from the nearest visible igneous rock, is worthy of special note. For the production of some of them, that is probably necessary. The hypothesis is proposed that these major joints were formed very soon after the intrusion of the igneous rock, at the beginning of a tectonic disturbance which widely affected the Triassic beds.

Among the species noted, the following call for special description :

Brookite.—Brilliant crystals, all less than a millimeter in length, but exceedingly well developed. This is the first reported occurrence of brookite in New Jersey. These crystals are transparent, showing a wide band of rich blue color in the direction of the brachydome zone, the portions on either side being amber-yellow. A similar blue color has been observed rarely in some octahedrites.

Certain of the brachydome faces appear frequently as very narrow, bright lines ; this is especially true of the base *c*, which never yields a good signal. Measurements of some forms, often repeated, in certain cases show a slight deviation from the theoretical angle which proves that the faces are slightly vicinal or "disturbed." Some rounding occurs, especially on the side faces of the brachydome zone. These crystals (see fig. 1) were measured on the Goldschmidt two-circle goniometer, with the following results :

Angles.

Forms	Letter	Symbol	Calculated		Xl 1		Xl 2		Xl 3		
			ϕ	ρ							
Base---	*c*	(001)	--	0	--	0	--	0	--	0	Minute
Brachydomes	*D*	(025)*	0	20 42	0	21 42	0	20 41	0	21 25	Fair
	d	(043)	0	51 32	0	50 02	0	49 56	0	50 59	Prominent
	t	(021)	0	62 06	0	63 02	0	62 32	0	61 58	Prominent
	T	(041)*	0	75 11	0	76 31	0	76 07	0	76 19	Rounded
Pinacoids	*b*	(010)	0	90 00	0	90 00	0	90 00	0	90 00	Rounded
	a	(100)	90 00	90 00	--	--	90 00	88 12	--	--	Minute
Prisms	*l*	(210)	67 10	90 00	67 30	90 00	66 22	90 00	--	--	Prominent
	L	(230)*	38 23	90 00	39 00	90 00	38 12	90 00	--	--	Fair
	p	(120)	30 43	90 00	--	--	--	--	30 23	90 00	Fair
Pyramid	*X*	?(313)*	74 20	49 22	--	--	75 18	49 00	--	--	Prominent

It will be noted that several of the forms (new forms are starred *) are new to the species. Especially noteworthy are the brachydomes, which fill in some of the gaps in the previously known series of these forms as follows:

((001)), (025),* (012), (089), (011), (043), (021), (041),* ((010)).

The harmonic series of symbols is apparently series N_4 of Goldschmidt:

0 (1/4), (1/3), (2/5), (1/2), (3/5), (2/3),
1, (4/3), (3/2), (5/3), 2, (5/2), 3, 4, inf.

Other new forms are the prism (230) and the doubtful pyramid ?(313).

All the brookite crystals so far found have come from a brecciated zone at Matthews' quarry, in the west end of Princeton.

Ilmenite.—Rosettes, of all sizes up to $\cdot 8^{cm}$ in diameter, composed of brilliant black hexagonal places arranged in nearly parallel position, giving an appearance similar to that of the "eisenrosen" found in Switzerland and elsewhere. Specimens from Princeton show only three forms, as follows: *c*, (0001); *m*, $(10\bar{1}0)$; *a*, $(11\bar{2}0)$.

Specimens from Byram, however, are richer in forms:

Dana		Goldschmidt		Calculated.		Measured.		
Letter.	Symbol.	Letter.	Symbol.	ϕ	ρ	ϕ	ρ	
c	(0001)	*c*	(0001)	--	0	--	0	Prominent
a	$(11\bar{2}0)$	*a*	$(10\bar{1}0)$	0	90 00	0	90 00	Prominent
m	$(10\bar{1}0)$	*b*	$(11\bar{2}0)$	30 00	90 00	30 00	90 00	Minute
π	(12.3)	π	$(10\bar{1}1)$	0	42 42	0	42 30	Minute
r	$(10\bar{1}1)$	*p*	$(11\bar{2}1)$	30 00	57 58	30 00	58 07	Prominent
e	$(01\bar{1}2)$	δ	$(11\bar{2}2)$	30 00	38 38	30 00	38 38	Fair
n	$(22\bar{4}3)$	λ	$(20\bar{2}1)$	0	61 33	0	61 37	Distinct

Fig. 3 shows a crystal with the above forms. Ilmenite of this type, showing the rosette arrangement, has been found in the quarries in the argillite at the east end of Princeton; in the Traction Co.'s quarry on the Pennsylvania side of the Delaware River in the vicinity of Scudders Falls; with massive analcite in the brook bed near the railroad station at Byram, N. J.; and in the railroad cut and argillite quarry near Rushland, Montgomery Co., Pa. Ilmenite also occurs at Princeton, and at Byram in the form of flat plates with bluish metallic lustre and rough outlines.

Analcite.—In the Princeton quarries, simple isometric form most typical of this species, the tetragonal trisoctrahedron or trapezohedron (211). At Byram, Hunterdon Co., N. J., white, cleavable masses, two inches thick, filling seams, in the brook bed. There are also in this latter material some crystals, all much flattened on account of their growth in a narrow cavity. An analysis of the massive mineral, by Prof. A. H. Phillips, gave:

Al_2O_3	23·58	per cent
Na_2O	14·35	" "
SiO_2	53·79	" "
H_2O	8·35	" "
Total	100·07	" "

This approximates closely to the average composition of typical analcite.

Barite.—From McCarthy's quarry, Princeton. Crystals of dimensions ranging up to $1^{cm} \times \cdot 5^{cm}$ and larger; translucent; color a delicate pink. The best crystal (fig. 2) obtained was measured, and was found to yield the following common forms: *m* (110), *c* (001), *a* (100), *u* (101), *d* (102), *o* (011), *z* (111), *y* (122).

Chlorite.—Dark green, minutely flaky masses of chlorite, resembling the variety known as delessite. It occurs in isolated masses on the analcite, enclosing ilmenite rosettes.

Pyrite.—Abundant; some complicated crystals in open cavities. One of these latter crystals, less than 1^{mm} in diameter, was of octahedral habit and showed the following forms: *p* (111), *a* (001), *d* (101), *n* (311), *e* (210).

Calcite.—One small crystal of calcite from Princeton, of rhombohedral habit, showed the forms: *r* ($10\bar{1}1$), *m* ($10\bar{1}0$), *c* (0001). A crystal from the northernmost quarry on the Pennsylvania side of the Delaware River, in the vicinity of Scudders Falls, was a combination of *e* ($01\bar{1}2$) and *m* ($10\bar{1}0$).

Quartz.—The Delaware River quarry (described under Calcite) afforded some well crystallized quartz. A crystal $\cdot 5^{cm}$ long and $\cdot 2^{cm}$ in diameter, transparent and doubly terminated, showed the following forms: *r* ($10\bar{1}1$), *z* ($01\bar{1}1$), *s* ($11\bar{2}1$).

Paragenesis of the Minerals.—The brookites and the ilmenites were the first minerals to form. Ilmenite probably was produced in most places because of the presence of iron in the solutions which could combine with the titanium. The brookites are found either attached to the matrix, or in analcite, the solution of which on entering the cavity carried away some of the crystals from their slender points of attachment. The ilmenite rosettes and the thick, irregular plates of ilmenite occur close together, and appear to have been produced at the same time. Sometimes there is an acicular, zeolitic mineral (species undetermined) which has grown directly on the ilmenite, and is at times surrounded by the analcite. It is monoclinic, showing pyramid, prism, and macro pinacoid. The analcite always surrounds the ilmenite and brookite when the latter minerals are present, and is itself covered with a layer of calcite, the latter often filling the balance of the cavity. The barite is found imbedded in calcite, and resting on analcite, but not penetrating it. Small pyrite cubes occupy a similar position. There are many cubes of pyrite in the black shales, which occasionally reach a diameter greater than one centimeter. They are always composite, being built up of nearly parallel crystals in rosette-like form. Chlorite of the kind described is a decomposition product of ferromagnesian minerals. The chlorite in the present deposit does not have the appearance of having resulted from the decomposition of another mineral in the present place; it may have been brought in by solutions.

Brown University, Providence, R. I.

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *The Transmutation of Elements.*—The alchemistic ideas of transmutation were apparently overthrown completely by the development of modern chemistry, until a few years ago, when it was found that the radio-active elements spontaneously decompose with the formation of helium and other elements. Sir William Ramsay and Soddy were the first to prove that helium is produced by radium, and since that time Ramsay has announced several transmutations of elements under the influence of the radium emanation, such as the production of lithium from copper, of carbon from silicon and thorium, and of neon from water. These alleged transmutations have been received with much incredulity by chemists and physicists, and it appears that the copper-lithium transformation has been shown to be without foundation by Madame Curie.

New developments have been made recently in the direction of apparent transmutation. At a meeting of the London Chemical Society, on Feb. 6, 1913, Sir William Ramsay read a paper on "The presence of helium in the gas from the interior of an X-ray tube," in which he states that there is no doubt that old X-ray bulbs contain helium, and he attributes its presence to its formation by the action of the electric discharge. There is room for doubt in regard to transmutation, but there seems to be no doubt that remarkable phenomena take place in the X-ray bulb, for at the same meeting Prof. J. Norman Collie and Mr. H. Patterson presented a paper on "The presence of neon in hydrogen after the passage of the electric discharge through hydrogen at low pressure." These two investigators had started their work independently from different points of view, and had collaborated when they found that they were getting the same results. Professor Collie had subjected fluorspar to the electric discharge with the hope of decomposing fluorine, and from the first experiments helium appeared to be formed in the bulb, while subsequent experiments showed the presence of neon. Further investigation showed the same result when calcium chloride and when glass wool were used, and finally even when the discharge was passed in the bare glass tube. Mr. Patterson started with the idea that the action of the discharge might change hydrogen to helium, but upon trying this he found neon. Then he filled his apparatus with pure oxygen, and upon pumping it out obtained the same result. He then surrounded his experiment tube with another containing neon, in order to find if this gas could penetrate the glass walls of the inner tube under the influence of the discharge, but obtained about the same result as with ordinary air. A similar experiment was made with helium with negative results. Lastly he used the outside tube as a vacuum which was higher than that used in the X-ray tube itself, and still found neon, the quantity thus obtained being comparable with that present in about 2 cubic centimeters of air. (This announcement is said to have been greeted with loud cheers at the meeting. It may be observed that this amount of neon is very small, corresponding to only about $\frac{1}{20000}$ cc. or 0·00000002 g.) Mr. Patterson repeated the experiment twice with the tube surrounded with a vacuum, and finally found helium mixed with neon in the outside vacuous tube. Ramsay accounts for the successive appearance of helium and neon in the tubes by suggesting that helium (4) plus oxygen (16) equals neon (20).

Sir J. J. Thomson has published a letter in regard to this matter. By using the method of positive rays, which is more sensitive than spectrum analysis and furnishes much more definite information about the gases, he has observed the appearance of helium and a gas of atomic weight 20, presumably neon, in discharge tubes, as well as a new gas of atomic weight 3, which he calls X_3, considers as possibly made up of three atoms of hydrogen, and which apparently does not occur in the atmosphere. He has found no connection between the appearance of these gases and the gas used to fill the bulb, but his experiments show that by bombarding various metals and other bodies with cathode rays these gases appear. His conclusions are different from those brought forward at the meeting of the Chemical Society, for he has found that, using iron wire terminals with an arc discharge, the gases appeared at first but diminished and finally failed to appear after the same terminals had been employed repeatedly, but with new terminals the gases appeared once more. He says, "This experiment seems to me to point very clearly to the conclusion that these gases were in the terminals to begin with, were removed from them by long-continued sparking, and were not produced *de novo* by the arc." He points out a remarkable difference between the liberation of these gases and the violent expulsion of helium by radio-active substances. After a sample of lead had been boiled in a vacuum, the residual metal still gave off the gases under the influence of the discharge, but they were removed by long-continued sparking.

We are forced to conclude from Thomson's results that the only transmutations of the elements thus far known are spontaneous, and that no case of artificial transmutation has been definitely established.—*Chem. News*, cviii, 78; *Nature*, Feb. 13, 1913.

H. L. W.

2. *An Active Form of Nitrogen.*—When a jar-discharge is passed through nitrogen at low pressure the gas retains a yellow glow after the discharge has stopped. This gradually fades away and disappears after about one minute. For some time Strutt in England has been investigating this phenomenon, and finds that the gas has remarkable properties. The glow gives a characteristic band-spectrum which is similar to the nitrogen spectrum obtained by using the uncondensed discharge, but not identical

with it. It is believed that the discharge converts ordinary nitrogen into an allotropic form, probably monatomic nitrogen, which reverts rapidly to ordinary nitrogen. The glow is regarded as the result of this reversion. The glowing nitrogen has some remarkable chemical properties. When it is passed through a tube containing a pellet of yellow phosphorus, a violet-reaction occurs, the glow is destroyed, red phosphorus is produced, and nitrogen is absorbed. In contact with iodine vapor at the ordinary temperature a magnificent light blue flame is produced. A reaction also occurs when sulphur or arsenic is gently heated in the glowing gas. Selenium, carbon, antimony, and hydrogen are without effect. When oxygen is admitted, the glow is quickly destroyed, but no combination takes place. If there is any trace of oxygen in the nitrogen that is used in the discharge tube, no afterglow takes place. With metallic sodium a little above its melting point in contact with the glowing nitrogen, the complete sodium spectrum is developed and nitrogen is absorbed. When the metal is heated to 250° C, the yellow line D becomes almost invisible and the green line E shows up strongly. There is also a reaction with mercury vapor, forming an explosive compound and developing the mercury spectrum. The reaction with nitric oxide is of particular interest. When this gas is mixed with the glowing nitrogen, a brilliant flame is produced and nitrogen peroxide is formed. This reaction is represented thus:

$$2NO + N = NO_2 + N_2.$$

Advantage is taken of this reaction to determine the percentage of active nitrogen in the glowing gas. An excess of nitrous oxide is added to it, and the mixture is led into a U-tube cooled by liquid air where the nitric oxide combines with more of the nitrous oxide, forming N_2O_3, which condenses as a blue liquid. From the weight of the trioxide the percentage of active nitrogen is calculated. The maximum amount found was 2·46 per cent. Active nitrogen reacts with acetylene, forming cyanogen, and with a large number of organic compounds containing halogens, forming in every case cyanogen and liberating the halogen. Certain substances, notably copper oxide and manganese dioxide, destroy the glow very quickly without undergoing any apparent change.

The effects of temperature are very remarkable. When the glowing nitrogen is led slowly through a tube cooled with liquid air, the glow is greatly increased in brilliancy and dies out before the coldest part of the tube is reached. When the gas is led through a tube moderately heated in one part, the glow is locally extinguished, but reappears beyond the heated part. If the glow is due, as assumed, to the reaction of monatomic nitrogen and the formation of the usual diatomic gas, there is here a negative temperature coefficient in connection with its velocity, and this is unique among known chemical reactions; but as no other reaction between monatomic elements has been studied, it is inferred that there may be a connection between the monatomic reaction and the negative temperature coefficient. It is possible to suppose that translational velocity in the atoms might be a hindrance to reaction. "If we permit ourselves the analogy of India rubber balls coated with some adhesive substance, the more violent the collision, the less likely it is that the balls will permanently adhere."—*Proc. Roy. Soc.;* Review by B. F. Lovelace, *Amer. Chem. Jour.*, xlix, 158. H. L. W.

3. *Interference of X-rays.*—Due to the combined efforts of W. Friedrich, P. Knipping, and M. Laue the vexed question concerning the nature of X-rays seems to have been settled once for all. Since it is a comparatively difficult matter to obtain a copy of the original papers, and since the work is of fundamental importance, the following account will probably not be considered too detailed or lengthy. In Laue's first mathematical paper it was shown qualitatively that if Röntgen rays are short electromagnetic pulses in the ether, then certain phenomena might be expected when a narrow pencil of X-rays was sent through suitable crystals. The considerations in this prophetic paper will be passed over and attention will now be directed to the experimental facts in the case.

A portion of the primary X-rays proceeding from an anticathode was allowed to pass through coaxial, cylindrical holes in four comparatively thick lead screens. In this way a pencil of primary rays of small cross-section was obtained. This pencil was then caused to pass through the crystal under investigation. The diameter of the hole in the lead screen nearest to the crystal was usually either $0{\cdot}75^{mm}$ or $1{\cdot}5^{mms}$. The crystal was mounted on the table of a goniometer since its orientation was found to be a matter of importance. Also everything had to be lined up very accurately with respect to the axis of the primary cone (practically a cylinder). Three photographic films and two plates were placed in the following positions: One film was set up $2{\cdot}5^{cms}$ in front of the incidence face of the crystal with its plane at right angles to the axis of the primary pencil. The two remaining films were adjusted parallel to the first but at distances of $3{\cdot}5^{cms}$ and 7^{cms} from the emergence face of the crystal. The two plates were disposed parallel to the primary pencil on opposite sides of the crystal and at the same distance, $2{\cdot}5^{cms}$, from the lateral faces of the specimen. Thus the pencil of primary rays registered circular black spots near the middle of each of the photographic films. Obviously the side plates were not struck by the primary pencil. When the crystal consisted of a carefully prepared and accurately adjusted specimen of zinc blende it was found, on developing, that the first film and the two lateral plates showed respectively only the central primary image and slight fog; in other words, nothing new or interesting. On the contrary, the two films beyond the emergence face recorded a large number of small dots which were distributed on circles concentric with the primary image. Each circle contained four pairs of equidistant dots which were located with perfect symmetry with reference to two mutually perpendicular axes. The dots on successive circles, however, alternated from one set of axes to a second set, so that the entire figure presented an eight-fold symmetry. Dotted figures were also obtained with crystals of copper sulphate, rock salt, galena, and diamond. The greatest attention was given to zinc blende because of its very simple crystallographic structure. In the case of the diamond the lateral photographic negatives contained black dots as well as the emergence films. As yet this apparent anomaly has not been explained. In all cases the figures on the more remote emergence film were exact enlargements of the figures on the film nearer the crystal, thus showing that the secondary radiation is propagated in straight lines. (It may be remarked that the necessary exposures lasted from 1 hour to 20 hours, and they were given intermittently to save the X-ray bulbs.)

The theory given in Laue's two papers agrees both qualitatively and quantitatively with the negatives obtained with zinc blende. The crystal is considered as made up of elementary cubes having molecules of sulphur and zinc at their vertices. Consequently the entire crystal is equivalent to a perfect three-dimensional diffraction grating. Also, the systems of photographic dots are analogous to the figures produced by crossed gratings, in the corresponding two-dimensional problem. When the primary X-rays pass through the crystal they cause the molecules (or their constituents) to send out secondary (fluorescent) X-rays which are in just the right condition for presenting interference phenomena, provided they consist in electromagnetic pulses and not in corpuscles of some sort or other. The negatives show the interference patterns and hence the conclusion must be drawn that the secondary radiation is of the short-wave type. It is also highly probable that the primary Röntgen rays are likewise ethereal pulses, but further investigation will be required to fully establish this hypothesis. The position of each of the dots on the negatives fulfils the three necessary conditions for maxima of luminosity. The loci of the directions in space which correspond to a difference in path from consecutive molecules of a whole number of wave-lengths are circular cones. The cones whose axes are at right angles to the axis of the primary pencil have very large semi-vertical angles, and they intersect the emergence films in two families of hyperbolas. The cones which are coaxial with the primary pencil meet these films in circles, of course. When two hyperbolas and a circle, all of the same order, meet in one and the same point there will be a maximum effect and a dot will be recorded on the film, if the exposure is adequate. It is necessary but not sufficient, in general, for two plane loci to intersect.

Assuming the number of molecules in a gram molecule or mol to be $6{\cdot}17 \times 10^{23}$, and the molecular weight and density of zinc sulphide as 97·4 and 4·06 gram/cm^3 respectively, the diameter of a molecule calculated from Laue's formulæ comes out to be $3{\cdot}38 \times$

$10^{-8\mathrm{cm}}$, which is in excellent accord with the values obtained by entirely independent methods. It is far more interesting and important to note that the wave-lengths of the secondary X-rays are of the order of $2\times10^{-9\mathrm{cm}}$. More precisely, Laue evaluates five wave-lengths whose coefficients of $10^{-9\mathrm{cm}}$ are respectively 1·27, 1·90, 2·24, 3·55, and 4·83. These numbers have approximately the ratios of the integers 4:6:7:11:15. It should be remarked, in conclusion, that the solutions are not single valued, and that the interference figures obtained by Friedrich and Knipping have been accounted for by W. L. Bragg on a somewhat different assumption concerning the distribution of atoms in the molecule, and by considering reflections from planes of atoms. The two theories, however, differ chiefly in the point of view and mode of attack, but fundamentally they amount to very much the same thing. — *Sitzungsber. d. K. Bay. Akad. d. Wiss.*, München, June, July, 1912. H. S. U.

4. *Researches in Colour Vision and the Trichromatic Theory;* by SIR WILLIAM DE W. ABNEY. Pp. xi, 418, with 100 figures and 5 plates. London, 1913 (Longmans, Green and Co.).—The author has brought together in book form the substance of a comparatively large number of communications on the subjects of color photometry and color vision, which he has made to the Royal Society during the last twenty-five years. A reference list of twenty-nine of these papers is given just before the index. The most cogent reason for issuing this work is the author's desire ". . . to show that the Trichromatic Theory of Colour Vision does not yet require a funeral oration over its remains." "It is not by any means as moribund as some seem anxious it should be considered, but is, in fact, very much alive."

The volume is divided into two Parts, of which the first is elementary and deals with such subjects as the eye, phenomena of vision, spectral colors, luminosity, color discs, etc. It is designed as an introduction to the more specialized and advanced portions of the text. The main subject of Part II is color vision and hence it treats of the physical theory of color vision, of color sensations, of congenital and other forms of color blindness, of retinal fatigue, and so forth. The author does not criticize any rival theory but confines himself to an account of his own researches. This book is an extremely important contribution to the subject, and it will undoubtedly be heartily welcomed by physicists, physiological psychologists, ophthalmologists, and others. The colored plates are beautifully tinted and no improvement in the typography seems possible. (However, in fairness to the lay reader, it should be remarked that the statement on page 3, to the effect that the number of pairs of spectra which a diffraction grating can produce is theoretically infinite, is incorrect.) H. S. U.

5. *Radium and Radioactivity*, (Romance of Science Series); by A. T. CAMERON. Pp. 185, with 23 figures. London, 1912 (The Society for Promoting Christian Knowledge).—A sufficiently

clear idea of the contents of this book may be obtained from the following quotation : "In this small volume an attempt has been made to deal with the most important facts of the science of Radioactivity in a manner simple enough to be understood by readers with a very elementary knowledge of Physics and Chemistry." On the whole, the treatment of the subject is reliable but rather one-sided, for, relatively too much space is devoted to the work of Sir William Ramsay. A typical illustration of this bias is afforded by Chapter VII which is entitled "The Transmutation of Elements," and which should be read with due caution and reservation. Also, the emanation from radium is called "niton" almost exclusively. The volume contains four useful appendices but no index. H. S. U.

6. *Spectroscopy ;* by E. C. C. Baly. Second edition. Pp. xiv, 687, 180 figures and 3 plates. London, 1912 (Longmans, Green and Co.).—Since the first edition (1905) of this book was the best text on the subject in the English language, and since numerous important spectroscopic investigations have been carried out during the past seven years, the new edition will be welcomed by all who are interested in this highly specialized branch of science. In order to save space, Chapter XVII of the earlier issue, which described Rowland's ruling engines, has been omitted. Also, other matters of relatively minor general importance have either been left out entirely or discussed very briefly. Nevertheless, the text proper has increased from 550 to 649 pages.

More specifically, the first nine chapters have only been changed by the addition of such material as brings them down to date. Chapter X has had its title and content altered from "The Efficiency of the Spectroscope" to "The Practical Resolving Power of the Spectroscope." In other words, Wadsworth's theoretical investigations have been omitted and replaced by Schuster's more useful results. Chapter XII, formerly on "The Production of Spectra," is now entitled "Methods of Illumination," and the articles on absorption spectra have been elaborated and collected in a new chapter, (XIV). In like manner, a separate chapter has been devoted to fluorescence and phosphorescence, (XIII). In the new edition, Chapters XVI, XVII, and XVIII have been very appreciably increased in scope, and excellent bibliographical lists have been appended to the last two of these chapters. It is clear therefore, that as far as the subject matter is concerned, the text has been markedly improved and its practical value as a reference book has been greatly increased. Unfortunately, in matters of detail, such as proof-reading and accuracy of statement, much room for improvement remains. H. S. U.

II. Geology and Mineralogy.

1. *The Eurypterida of New York;* by John M. Clarke and Rudolf Ruedemann. New York State Mus., Mem. 14, 2 vols., 638 pp., 88 pls., 121 text figs., 1912.—This monograph on the Eurypterida of America—for it treats of all American forms—is truly a monumental work and a model for all paleontologists to follow, provided they have a liberal state treasury back of them. In this work one can study Eurypterida from any viewpoint permitted paleontologists. Here we may find their chronology, their development from baby stages prophetic of unknown ancestors to adults, and their relations to scorpions, horse-shoe crabs, trilobites, and even to the hypothetic annelids. The volume of plates is not only a storehouse of merostome information but as well a work of art. In it the text-book writer will find the animals pictured true to life and easy of incorporation as text figures.

An adequate summary of the results obtained cannot be given here, but only a few of the striking ones picked out here and there. The oldest reported merostomes are those of late Proterozoic time (Belt formation), known as *Beltina danai* Walcott. Regarding them the authors state: "We entertain no doubt that these bodies, or the greater part, are of organic origin and while unable, after careful study, to convince ourselves that they are merostomatous, yet to renewed efforts in the field they do give promise of a recognizable fauna" (386). Regarding the remarkable Middle Cambrian forms they write: "It seems to us probable that the Limulava as described are not eurypterids, but constitute a primitive order, though exhibiting some remarkable adaptive features. This order possibly belongs to the Merostomata but it is distinctly allied to the crustaceans in such important characters as the structure of the legs and telson, and is therefore much generalized" (410).

Much has been written about the habitat of these animals, and as Clarke and Ruedemann have seen more material than any other paleontologists their opinion has added value. They say:

"Summarizing these data we conclude that the eurypterids lived in the sea from Cambric to Siluric time. They had then become less sensitive to changes, positive and negative, in the salinity of the water. In fact they seem to have thrived best under conditions of life that exclude most other marine groups of animals, that is, in the marginal, more or less inclosed marine lagoons, accompanied by estuaries receiving delta-forming terrestrial drainage, with prevailing arid or subarid climate, the waters being in some places more than normally briny, in others having less than normal salinity. In other words they were *euryhaline* or able to live in both salt and brackish water. . . . Thus while the earlier eurypterids were marine and their climacteric fauna euryhaline; their later habit throughout the Devonic and Carbonic led them finally into the fresh water" (112).

Concerning the early stages of growth and the larvæ of scorpions, they sum up as follows :

"We consider as coenogenetic or purely larval the relatively larger size of the carapace, of the compound eyes and of the swimming legs, and the smaller number of the abdominal segments ; as palingenetic and phylogenetic, the approximation of the compound eyes to the margin, the prominence of the ocelli and their tumescences, the lack of differentiation of the abdomen and the smaller size of the telson. In these palingenetic characters the nepionic stage resembles so much the Cambric Strabops, that we shall designate this as the *Strabops stage*" (122-3).

"We may say that, (1) the general homologies of the two [embryonic and larval stages of the scorpion and the larvæ of the eurypterids] are very apparent in the composition of the carapace and abdomen of an equal number of segments, but that, (2) while in the scorpion the segmentation is completed long before the hatching, in the eurypterids the larvæ in the nepionic stage still lack the full complement of segments, recalling the trilobites in this feature and clearly representing a more primitive condition ; (3) there are a number of distinct differences in the larvæ of the eurypterids and of the scorpions, some of which lie in the form of the carapace, the early embryonic differentation of the pedipalps from the other appendages, the strong prelarval differentiation of preabdomen and postabdomen and the disappearance of the abdominal appendages in the scorpions and their persistence in the eurypterids" (145-6).

"The early appearance and later atrophy of the abdominal appendages is clearly a feature that points to a common ancestor for the scorpion and the eurypterids having such appendages, and we believe that the cephalothorax in the embryo of the scorpion retains ancestral features from the facts that its length corresponds to about six abdominal segments and it equals the latter in width ; that, however, the strong development of the procephalic region is tachygenetic.

"A comparison of the larvæ of all three, the eurypterids, Limulus and the scorpion, shows both the latter to have lost the primitive form of the abdomen by acceleration, that of Limulus being much broadened, that of the scorpion abruptly contracted to the tail or postabdomen while the eurypterids have best preserved the original gradual and uniform contraction. The carapaces of the eurypterids and the scorpion have most nearly retained the original proportions and form of the common ancestor. Of the cephalothoracic appendages the chelicerae are alike in all three groups and obviously ancestral in their form ; the remaining legs have taken quite different courses of adaptation, the scorpions having developed the powerful chelate pedipalps, the eurypterids the swimming legs, while those of Limulus have remained relatively undifferentiated, and show no tachygenetic features in the embryos except the chelæ. The embryo of the scorpion shows simple walking legs, like those of the eurypterids, and lacks the two movable claws. This simple form of the walking leg is also exhibited in a very remarkable manner by the Siluric Palæophonus. It is quite safe to infer that this is the form of the cephalothoracic appendages inherited from the common ancestor.

"A corollary of these inferences is that neither Limulus nor the scorpions is derivable from the eurypterids, but that all three, while related, have early separated ; and that the eurypterids are still nearest in their general aspect to this common ancestor. . . . There is no reason to doubt that, as there are eurypterids in the Cambric, the scorpions also reach back to that era and the diversion from the common ancestor must have already been inaugurated in early Cambric time" (146-7).

"As the most primitive and earliest crustaceans, the trilobites, are clearly not ancestrally or otherwise closely related to the eurypterids and the latter even in the Cambric are far removed from any possible synthetic ancestors, it is a fair question whether it is not proper to look for more primitive arthropods than the crustaceans as ancestors of the eurypterids. . . . Bernard derives the Crustacea from a bent carnivorous annelid, a view which Beecher regards as partly verified by his discoveries concerning the ventral anatomy of the trilobites, and it is therefore worthy of consideration in this place. If we consider the absence of anything in the ontogeny of the eurypterids that would suggest a crustacean nauplius stage, the admitted absence of all crustacean features in the adult forms, and the equal absence of all crustacean features in the ontogenies of Limulus and the scorpion, it becomes manifest that the inference of the derivation of these classes from arthropods more primitive than the Crustaceans, seems well founded" (148-9). C. S.

2. *Correlation of the Devonian system of the Rock Island region ;* by W. ELMER EKBLAW. Trans. Ill. Acad. Sci., 5th Ann. Meeting, Feb. 23, 24, 1912, 15 pp., 2 figs.—An excellent short paper listing according to the individual beds 109 species of the higher Middle Devonian as exposed in Rock Island and Henry counties, Illinois. This fauna is clearly of the Dakotan province, as 83 per cent of the determined forms are common to these two western areas. C. S.

3. *Untermeerische Gleitung bei Trenton Falls (Nord-Amerika) und ihr Verhältnis zu ähnlichen Störungsbildern ;* by F. FELIX HAHN. Neues Jahrb. für Min., Geol. u. Pal., Beilage-Bd. xxxvi, pp. 1-41, pls. I-III, 1912.—A valuable paper explaining local crumpled beds, edgewise conglomerates, and in part intraformational conglomerates, as due in the main to slipping of the deposits, while still soft or but little consolidated, on slight inclines of the sea bottom. Many examples are given in formations throughout the geologic column. This interpretation has a direct bearing on the significance of disconformities. C. S.

4. *Iowa Geological Survey ; Vol. XXI, Annual Reports, 1910 and 1911,* with accompanying papers, prepared in coöpera-

tion with the United States Geological Survey; GEORGE F. KAY, State geologist. 18 plates, 7 figs. Des Moines, 1912.—The lines of investigation now being carried on by the Iowa Survey include: a study of road materials under the direction of Dr. Beyer; an examination of the Aftonian gravels with their interesting mammalian fauna by Professor Shimek; mapping of the Wisconsin drift by Professor Carman; steam gaging, topographic mapping in coöperation with the Federal Survey, detailed geologic mapping and the preparation of physiographic monographs for educational purposes. The announcement is made that a volume by Dr. Hay on the Pleistocene mammalian fossils of Iowa is nearing completion. Volume XXI is almost wholly (pp. 31–1186) devoted to Professor Norton's report on the Underground Water Resources of Iowa. This paper (published also by the U. S. Geological Survey as Water-Supply Paper No. 293) constitutes the most thorough and extensive study dealing with a single state so far published. Not only are the geologic principles governing groundwater amply discussed, but with the aid of a large corps of assistants, Professor Norton has made examinations of local conditions to such an extent that districts, cities, and frequently owners of individual farms are supplied with data directly applicable to their needs. The appropriations for the Iowa Survey are justified on the strength of this volume alone. H. E. G.

5. *Bureau of Economic Geology and Technology, Texas,* WM. B. PHILLIPS, Director. A Reconnaissance Report on the Geology of the Oil and Gas Fields of Wichita and Clay Counties, Texas, by J. A. UDDEN assisted by D. McN. PHILLIPS. Pp. xiv, 308; 26 plates, 8 figs., map in pocket. Bull. Univ. Texas, No. 246, Sci. Ser. No. 23, September, 1912.—The geologic study of an oil field involves minute description of local dips, careful determination of rock textures and composition, and exhaustive study of drill cores, subjects to which the major part of the present report is devoted. The bulletin also includes the results of the Wichita formation based on extensive field observations. The Wichita shales, the sandstones, conglomerates, the Beaver-burk limestones, and the Bluff bone-bed are discussed in their stratigraphic and structural aspects and lists of fossils are given.

H. E. G.

6. *Wisconsin Geological and Natural History Survey, Bulletin XXV, Sci. Ser. No. 8, 1912. Sandstones of the Wisconsin Coast of Lake Superior;* by FREDRIK TURVILLE THWAITES. Pp. viii, 117; 23 plates, 10 text figs., map in pocket.—A study of the bed rock geology along the shore of Lake Superior from Duluth to Hurley has resulted in an increased amount of petrographic structural detail, a modification of former views, and in the production of a map based chiefly on lithologic characters. The two large groups into which the red sandstones have been divided are shown to be conformable, the upper (Bayfield group) consisting of nearly horizontal quartz sandstone, and the lower (Oronto group) being phases of a period of continuous or slightly

interrupted deposition. Both series are assigned to the upper Keweenawan and are believed to have been deposited subaerially in a basin formed by folding of earlier Keweenawan strata. The contact of the Bayfield groups with the Middle Keweenawan traps is described as a fault. The basin of Lake Superior at its western end is interpreted as the result of differential erosion.

H. E. G.

7. *State Geological Survey of Wyoming, Bulletin 4, Series B, The Salt Creek Oil Field, Natrona County;* by C. E. JAMISON, State Geologist. Pp. 75; 16 plates, map in pocket, 1913.—The Cretaceous formations—Dakota to Laramie—represented in central Wyoming have been described by Darton, Stanton and Knowlton, and a paper on the Salt Creek Oil Field by C. H. Wegemann was published by the U. S. Geol. Surv., Bulletin No. 452. Mr. Jamison, in the report under review, adds certain structural and petrographic detail, particularly with regard to the oil-bearing sands. A description of the present stage of development of the field, which has already produced 2,500,000 barrels, constitutes the larger part of the bulletin. H. E. G.

8. *State Geological and Biological Survey of South Dakota, Bulletin No. 5, 1912, The Geography, Geology, and Biology of South Central South Dakota;* by E. C. PERISHO and S. S. VISHER. Pp. 152, 44 plates, 5 maps, and geological chart.—While of a reconnaissance nature, the report of Perisho and Visher constitutes a praiseworthy contribution to our knowledge of "bad lands" and sandhill in a region somewhat unique. The topics treated, including climate, soil, topography, water supply, ecology, etc., give the paper a geographic aspect and make it of general interest. The reproduction of numerous photographs increases its attractiveness in this regard. The geological chapters contain those features most desirable in a preliminary report, viz., recognition of the larger stratigraphic units, description of the more common fossils, composition and areal distribution of distinctive beds, combined with a discussion of the views of previous workers in the field. H. E. G.

9. *Brief Notices of some recently described Minerals.*—BETAFITE, SAMIRESITE, AMPANGABEITE, MANANDONITE are names given by A. Lacroix to new minerals from the remarkable pegmatite localities recently exploited in Madagascar. Of these betafite from Ambolotora and samiresite from Samiresy are allied to the Swedish species blomstrandite, which also occurs at Tongafeno. All these last species are isometric in crystallization and contain uranium in considerable amount and are hence radioactive; other bases are present in small amount. For the blomstrandite Pisani found 23·30 Nb_2O_5, 28·50 Ta_2O_5, 10·87 TiO_2; for betafite, 34·80 Nb_2O_5, 18·30 TiO_2; for samiresite, 45·80 Nb_2O_5, 3·70 Ta_2O_5, 6·70 TiO_2; it also gave 7·35 PbO while the others gave 4·00 and 3·45 CaO respectively.—*Bull. Soc. Min.*, xxxv, 84, 234, 1912.

AMPANGABEITE occurs in large rectangular crystals of a brown color; specific gravity 4·29. Analysis gave 34·80 Nb_2O_5, 8·90

Ta_2O_5, 4·90 TiO_2 with 19·40 UO_2, 8·60 Fe_2O_3 and 4·00 $(Y,Er)_2O_3$; its relations are uncertain though the material was homogeneous. —*Ibid.*, xxxv, 194.

Manandonite forms white lamellæ or mammillary crusts on quartz; cleavage micaceous; luster pearly. An analysis by Pisani gave: SiO_2 25·20, Al_2O_3 47·02, B_2O_3 9·25, Li_2O 3·97, K_2O 0·20, Na_2O 0·48, H_2O 14·10 = 100·22. The formula calculated is $H_{24}Li_4Al_{14}B_4Si_6O_{53}$. *L.c.*, p. 223. The Madagascar localities have also yielded many rare species including euxenite, monazite, columbite, strüverite, rhodizite, danburite, hambergite, bismuthinite, lazulite and others.

Plumboniobite is a niobate of uranium, yttrium, lead and other bases described by Hauser and Finkh from the mica mines of Morogoro, German East Africa. It occurs in massive form; color dark brown to black: hardness 5—5·5; specific gravity 4·81. —*Zs. anorg. Chem.*, lxiv, 2270, 1909, in *Zs. Kryst.*, li, 385.

Uhligite is described by O. Hauser as occurring in black octahedrons in a nephelinite on the Magad lake in East Africa. It is allied to keilhauite and zirkelite.—*Zs. anorg. Chem.*, lxiii, 340, 1909, in *Zs. Kryst.*, li, 320.

Vrbaite is a new thallium mineral described by B. Ježek from Allchar in Macedonia, and named after Prof. Vrba of Prague. It occurs in small pyramidal orthorhombic crystals; color bluish gray-black; hardness 3·5; specific gravity 5·3. An analysis by Křehlik yielded the formula $TlAs_2SbS_5$. *Zs. Kryst.*, li, 363, 379, 1912. Associated with the above mineral are orthorhombic crystals resembling stibnite in aspect which have been minutely studied and shown to be distinct in form, although material for analysis is not available. This has been provisionally named Allcharite.—*Ibid.*, li, 275.

Preslite–Tsumebite. A new mineral from Tsumeb in German Southwest Africa has been described about the same time as preslite by V. Rosický and tsumebite by K. Busz. It occurs in small tabular crystals, often twins, referred by the first author to the orthorhombic system, by the second to the monoclinic system. Color green; hardness 3·5; specific gravity 6·1. Analysis showed it to be a complex basic phosphate of lead and copper. —*Zs. Kryst.*, li, 521, 526, 1912.

Baeumlerite is described as a new potash mineral by O. Renner. It occurs associated with halite and tachhydrite at the potash mine Desdemona in the Leinetal. The composition is stated to be $KCl.CaCl_2$.—*Centralblatt Min.*, p. 106, 1912. Zambonini later shows that it is identical with Scacchi's chlorocalcite. —*Ibid.*, p. 270, 1912, and *Min. Vesuv.*, p. 50, 1910.

Hatchite is a new mineral from the Binnenthal, Switzerland, described by R. H. Solly and G. F. Herbert Smith. Known only from a few small crystals of lead-gray color and distinctive triclinic form; composition undetermined.—*Min. Mag.*, xvi, 287, 1912.

Chrom-brugnatellite is allied to brugnatellite but contains chromium. It is described by Dr. Laura Hezner as occurring in violet-colored scales in the serpentine of Dundas, Tasmania. Analysis led to the formula, $2MgCO_3.5Mg(OH)_2.2Cr(OH)_3.4H_2O$. —*Centralblatt Min.*, p. 569, 1912.

ARDUINITE from the Val dei Zuccanti in Venice, now named by E. Billows, is a zeolite earlier referred to a red natrolite and to stilbite. Analysis by Billows gave: SiO_2 49·40, Al_2O_3 14·57, CaO 6·57, Na_2O 11·77, K_2O 1·54, Fe_2O_3 and Mn_2O_3 2·43 = H_2O 13·85 = 100·13. For this the formula $H_{16}Na_4CaAl_2Si_8O_{30}$ is calculated.—*Rivista Min. Crist. Ital.*, vol. xli, 1912.

PALAITE, STEWARTITE, SALMONSITE, SICKLERITE are new manganesian phosphates briefly described by W. T. Schaller from the tourmaline locality near Pala in Southern California, the first three from the Stewart mine, the fourth from the Vanderburg-Naylor mine. Palaite is a flesh-colored crystalline mineral (monoclinic ?) resulting from the alteration of lithiophilite; formula $5MnO.2P_2O_5.4H_2O$. Stewartite has a similar origin, is probably triclinic and while the material did not admit of the determination of its composition, the form and optical properties show it to be new. Salmonsite is derived from hureaulite and has the composition $Fe_2O_3.9MnO.4P_2O_5.14H_2O$. Sicklerite occurs in brown cleavable masses derived from lithiophilite; formula $Fe_2O_3.6MnO.4P_2O_5.3(Li,H)_2O$.—*Journ. Wash. Acad. Sci.*, March 19, 1912. A full description follows later in a Geol. Survey Prof. Paper on "The Gem Tourmaline Field of Southern California."

ARSENOFERRITE is iron disulphide, $FeAs_2$, in octahedral crystals with the pyritohedron, (310), and hence allied to pyrite. It is described by H. Baumhauer from the Lercheltiny Alp in the Binnenthal, Switzerland. An analysis by Schneider gave: As 71·10, Fe 28·90 = 100.—*Zs. Kryst.*, li, 143, 1912.

HOKUTOLITE is a radio-active mineral described by Y. Okàmoto; it occurs as a crystalline incrustation in the hot waters of the creek of Hokuto in Taiwan, Formosa. It consists chiefly of the sulphates of lead and of barium in varying proportions but whether as an isomorphous mixture or as layers of the different compounds is not certain. The mineral varies in color from white to yellow and brown; the specific gravity was found to be 6·1.—*Minerals of Taiwan*, p. 22, 1912.

10. *Text Book of Petrology; The Sedimentary Rocks;* by F. H. HATCH and R. H. RASTALL. 12mo, pp. 425; 60 figures. London, 1913 (George Allen and Co.).—This work is intended as a companion volume to that on igneous rocks published in 1909 by Dr. Hatch, though by a different publisher. This fact and the nature of the work make the title somewhat misleading, since the sedimentary rocks themselves are not classified and described. The book is, in fact, devoted to a discussion of the processes by which sedimentary rocks and their metamorphic derivatives have been formed, and is thus rather a work on their petrogenesis than on their systematic petrology. This may be seen from a consideration of the table of contents, in which successive chapters treat of: deposition in general; fragmental, chemical, and organic

deposits, that is the ways in which these are formed and the nature of the sediments ; metamorphism is then discussed, first in a general manner and then special phases, such as cementation and metasomatism, contact and regional metamorphism and, finally, weathering. At the end is an appendix in which methods of separation and determination of the minerals occurring in sands, clays and soils are summarized by Mr. T. Cook.

The nature of the work being understood, it will be found a very convenient elementary treatise for the student of petrology in setting out clearly and concisely the important processes and principles to which the sedimentary rocks owe their origin. It naturally suggests itself that the work should be followed by another in which the classification and petrographic description of the sedimentary and, possibly, metamorphic rocks would be undertaken to complete the series, and possibly this is hinted at in the preface, though not definitely promised by the authors.

L. V. P.

III. Miscellaneous Scientific Intelligence.

1. *Carnegie Institution of Washington;* Robert S. Woodward, President. *Year Book, No. 11, 1912.* Pp. xvii, 294 ; 7 plates, one text figure. Washington.—The completion of the first year of the second decade of the Carnegie Institution serves to show more definitely than heretofore what it has already accomplished and what are the most useful fields for its resources. Its history has proved that there is ample place for such an establishment devoted exclusively to the encouragement of research, on a broad and liberal scale, and this without interfering with other institutions already founded. The magnitude of the enterprise, as at present developed, is impressive, its total receipts from endowment and minor items amounting since 1902 to more than $7,000,000. During the past year the total sum expended was $1,148,000, of which about $520,000 was devoted to the large departments now firmly established, $103,000 to minor projects and research associates, and about $44,000 each to publications and administration.

Of the various departments to which the income of the Institution is chiefly devoted, much the largest amount has gone to the building and equipment of the Solar Observatory on Mt. Wilson, California, of which Dr. George E. Hale is director. The activity and wide range of work in this department is shown by the fact that the statement of the results of the past year involves a discussion of some thirty-five different subjects, many of them of first importance in astronomical research. Next to this comes the Geophysical Laboratory, under Dr. Arthur L. Day, the work of which is also reviewed in detail. A number of contributions from this laboratory have been published in the pages of this Journal through the year. A new line of research is noted which promises important results, quite different from those which have given the laboratory its reputation thus far, namely, the investigations of the physics and chemistry of active volcanoes. For example, specimens of gases collected from the crater of Kilauea, made by members of the staff, have been brought to the laboratory and much may be expected from their detailed study. The other departments have shown like activity, that of Botanical Research having included investigations in the Algerian and Libyan deserts. The non-magnetic ship *Carnegie*, in charge of Dr. L. A. Bauer, has traversed some 28,000 miles in the Indian and Pacific oceans during the year. The department of Meridian Astronomy has carried on its work, but unfortunately has met with a great loss by the death of its director, Dr. Lewis Boss. One of the recent developments of the Institution has been the attaching of eminent specialists to the force of the departments for limited periods of time. Eight such specialists have been employed during the past year, and the plan is regarded as having worked very satisfactorily. The wide distribution of the publications of the Institution since its foundation is indicated by the total of 100,869 volumes, which have gone out chiefly as gifts, but also to some extent as sales.

2. *Publications of the Carnegie Institution.*—Recent publications of the Carnegie Institution are noted in the following list (continued from vol. xxxiv, p. 493):

No. 74, Vol. VI. The Vulgate Version of the Arthurian Romances, edited from Manuscripts in the British Museum by H. OSKAR SOMMER. Pp. 391.

No. 90 A. Guide to the Materials for American History, to 1783, in the Public Record Office of Great Britain. Volume I, Pp. xi, 346. The State Papers, by CHARLES M. ANDREWS.

No. 159. The Mosquitoes of North and Central America and the West Indies; by LELAND O. HOWARD, HARRISON G. DYAR, and FREDERICK KNAB. Volume I. Pp. vii, 520; 14 plates. Vol. II, pp. x, 150 plates.

No. 170. The Electrical Conductivity, Dissociation, and Temperature Coefficients of Conductivity from Zero to Sixty-five Degrees of Aqueous Solutions of a number of Salts and Organic Acids; by HARRY C. JONES, assisted by various experimenters. Pp. iv, 148.

No. 171. Pierre du Ryer, Dramatist; by HENRY C. LANCASTER. Pp. v, 182.

No. 174. Easter Island. The Rapanui Speech and the Peopling of Southeast Polynesia; by WILLIAM CHURCHILL. Pp. 340.

No. 175. Researches of the Department of Terrestrial Magnetism. Land Magnetic Observations, 1905–1910; by L. A. BAUER. Pp. 185; 10 plates, and numerous figures.

No. 176. Study of Metabolism in severe Diabetes; by FRANCIS G. BENEDICT and ELLIOTT P. JOSLIN. Pp. vi, 135.

The Classics of International Law; edited by JAMES B. SCOTT. Works of Grotius. Vol. I. Text of 1646. Pp. 618. Works of Balthazar Ayala, 1581. Vol. I. Pp. xxvii, 227; vol. II, pp. xii, 250.

3. *Man: A History of the Human Body;* by ARTHUR KEITH, M.D., LL.D. Pp. 256. New York (Henry Holt and Company); London (Williams and Norgate).—A concisely written account of the natural history of man, his structure, ancestry, development, relationships, and racial peculiarities. The introductory chapters contain a brief description of the bodily structures, with particular emphasis on the characters of the brain, followed by an interesting discussion of man's place among animals. Stature, proportions, and posture are next considered, then the tail and numerous other vestigial structures which show man's kinship with other groups of animals. A brief description of the development of the embryo and of the organ systems of the body leads to a discussion of the evidence which malformations and monsters afford as to man's past history. Changes in the body during youth and age, sexual characters, and racial characters are treated in such a way as to furnish convincing evidence that the human species is still in process of evolution, while the concluding chapters treat of the bodily features as indexes of mental character, the skin, glands, hair, and sense organs, the wonderful mechanism which adapts all the organs to the functions which they are called upon to perform, the signs of degeneration, the capabilities of regeneration of parts, the antiquity of man and his genealogy.

This little book has the double merit of containing a vast amount of useful information in small compass and presenting it in an entertaining manner. W. R. C.

4. *The Growth of Groups in the Animal Kingdom;* by R. E. LLOYD, M.B., D.Sc. Pp. vii, 185, with two colored plates. New York and London, 1912 (Longmans, Green and Co.).—The author states that "the aim of this small book is to lessen the belief in Natural Selection as a creative agency," and to offer in its place further support for the theory of the origin of species by mutation. To this end he presents a number of somewhat disjointed essays discussing the instability of species, the absence of definite criteria by which they may be distinguished, and their possible origin by the growth of groups of individuals of similar characters.

The evidence is supported by the results of a study of the rats of India, by a critical review of Tower's work on the potato beetle, and by an examination of only twenty-two individuals of a genus of fishes. The new data which the book contains form an important contribution to the science of genetics, but the philosophical arguments in the concluding chapter can hardly be expected to gain any new converts to the mutation theory.

W. R. C.

5. *Genetics: An Introduction to the Study of Heredity;* by HERBERT EUGENE WALTER. Pp. xiv, 272; 72 figures and diagrams. New York 1913 (The Macmillan Company).—Out of the world-wide experiments in animal and plant breeding of the past decade has arisen the new science of genetics. The application of the newly-discovered laws of inheritance has already modified the practical breeding of domesticated animals and

plants, while the studies of heredity in the human race have suggested rational means for the perpetuating of desirable modifications and the elimination of unsuitable strains.

This book contains a well-written summary of the topics which comprise this science of heredity. The carriers of the heritage, variation, mutation, acquired characters, the pure line, segregation and dominance, reversion to old types and the making of new ones, blending inheritance, determination of sex, the application to man, and human conservation are the titles of chapters and indicate the general scope of the work.

The subject is clearly presented, and with the aid of the illustrative diagrams should prove of interest to the general reader without special biological training. W. R. C.

6. *Fatty Foods ;—their Practical Examination. A Handbook for the Use of Analytical and Technical Chemists ;* by E. RICHARD BOLTON, F C.S., and CECIL REVIS. Pp. xi, 371. Philadelphia, 1913 (P. Blakiston's Son & Co.).—This manual is primarily for the use of food analysts and is essentially devoted to the methods of extraction and identification applicable to fats. It contains numerous data regarding the most diverse fat-yielding products of both animal and vegetable origin, including in particular the constants to which reference is so frequently necessary in analytical procedures. The methods of examination include the routine familiarly practiced in most food laboratories, the details being dictated by the personal experiences of the authors. One notes the inclusion of a number of products, mostly of Eastern derivation and exemplified in shea nut oil, Djave butter, Latifolia and Longifolia fat, niger seed oil, candle nut oil, etc., not presented ordinarily in more elementary books on this subject. Milk products and feeding stuffs receive consideration beyond that which their fat content requires. The book may be designated as one of "selected methods" evidently determined in part by British requirements. L. B. M.

OBITUARY.

DR. JOHN SHAW BILLINGS, director of the New York Public Library, died on March 11 in his seventy-fourth year. Receiving his medical degree in 1860, he almost immediately began active practice as a surgeon in the civil war ; his excellent work during this period brought him rapid promotion in rank. Later he was attached to the Surgeon-General's office in Washington and in 1875 took charge of the library, developing it with great skill and energy. His index catalogue of this library was a monumental work published in 16 volumes (1880–1894). He had charge of the vital statistics of the 10th and 11th Censuses. In 1883 he became curator of the Army Medical Museum and Library, and retained this post until his retirement as lieutenant-colonel and deputy surgeon-general in 1895. In 1896 he became director of the New York Public Library, Astor, Lenox, and Tilden Foundations, and this position he held until his death ended a life of rare activity and usefulness.

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VOL. XXXV. MAY, 1913.

Established by **BENJAMIN SILLIMAN** in 1818.

THE
AMERICAN
JOURNAL OF SCIENCE.

FOURTH SERIES

VOL. XXXV—[WHOLE NUMBER, CLXXXV].

No. 209—MAY, 1913.

NEW HAVEN, CONNECTICUT.
1913.

THE TUTTLE, MOREHOUSE & TAYLOR CO., PRINTERS, 123 TEMPLE STREET.

Published monthly. Six dollars per year, in advance. $6.40 to countries in the Postal Union; $6.25 to Canada. Remittances should be made either by money orders, registered letters, or bank checks (preferably on New York banks).

THE

AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

Art. XXXIX.—*Subsidence Phenomena at Kilauea in the Summer of 1911*; by Frank A. Perret.

A column of liquid lava filling the conduit and reaching the crater of a volcano, and, therefore, in communication with the atmosphere, is, like the mercury of a barometer, in a condition of balance, and the same may be said of the *rate of emission* of its gases. It is, in a way, comparable to a steam engine lifting a load against gravity and exhausting against atmospheric pressure, in which any variation in the head of steam, or in the load, or in back pressure against the exhaust, would have a direct effect upon the work done. And, inasmuch as the height of the lava and the rate of gas flow directly affect the volcanic edifice and concur in the initiation of actual, external eruption, it behooves the volcanologist to study the variations of the lava column in connection with every possible cause, whether endogenous, superficial or extra-terrestrial.

During July, August and September, 1911, the height of the Kilauea lava column was taken by daily triangulations from the writer's observing station and abode on the east brink of Halemaumau, and from these a curve has been plotted as reproduced in fig. 1. The variations in the height of the lava, as shown in the curve, are expressed by the column of figures at the left in *meters below the station.* From these it will be seen that a rise of five meters in the early part of July brought the lava to the "high water mark" for this season, when it stood at seventy meters below the brink—an elevation which approximates 1114 meters above the sea. From this time to the end of September there was a general subsidence of the lava column, amounting to more than fifty meters, the abnormalities of which, with their causes and their immediate effects, are briefly examined in the present paper.

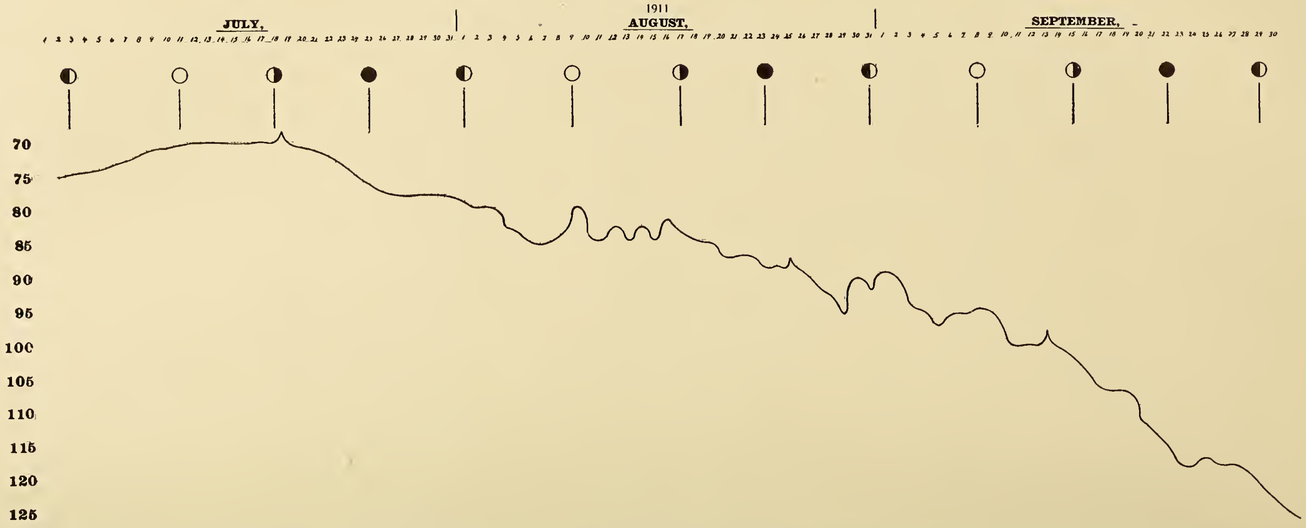

Fig. 1. Curve showing variations in height of the lava column for three months. Figures indicate meters below the edge of the pit.

Reference to the curve will show the first abnormality to have been a sudden upward oscillation of the lava in the night of July 18th, with repetitions on August 25th and September 13th. These consisted of a phenomenal irruption of gas from below, temporarily raising surface conditions to the super-normal grade of activity and causing a rise—almost momentary in its duration—of some two meters in the level of the lake. Each of these gaseous outbursts was followed by a very considerable subsidence of the lava column, as will be seen from the curve, and the phenomenon is, in all probability, purely endo-volcanic, having its cause in the depths of the conduit. If we consider this as widening out into its parent fissure at no great depth it is easy to imagine gas retention in the latter and, from time to time, an escape into the conduit. That an accumulative process is involved seems indicated by an apparent periodicity in these outbursts, the interval between the last two being double that of the first. The writer finds, moreover, on consulting his notes, that a repetition of this phenomenon, but on a very small scale and not observed by him, was reported to have occurred in the night of August 6th, when the lake surface was said to have suddenly risen "about one foot," with considerable agitation. At the time of plotting the curve this event was not considered of sufficient magnitude to be introduced, but, admitting it as an actual recurrence of the phenomenon, we have a regular series of these gaseous irruptions with a period of about eighteen days. That of August 25th was coincident with a series of local seismic disturbances, four shocks preceding and two following the outburst of gas and the entire period of general agitation lasting from 6.30 A. M. to 2.35 P. M. The absence of seismic effects at the times of the three remaining oscillations forbids our considering the earthquake as the cause—temptingly easy on the theory of the concussion causing coalescence of the smaller gas vesicles distributed through the lava, by which means, alone, these may acquire effective dynamic properties—and makes it consequent or concomitant to the gaseous outburst. These rapid oscillations of the lava were instrumental in the sinking of the floating island of 1911, as described in the paper on that subject.*

The effect of atmospheric pressure variations upon the column of lava is, as a rule, more apparent in its control of the rate of gas flow than in any observable variation in the height of the lava column excepting as this is influenced by the rise and escape of the gas. The case of Stromboli is well known, but all the Italian volcanoes—especially when in the condition of actual eruption—show increased activity on a decrease of atmospheric pressure, even the diurnal minima exerting an

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* This Journal, March, 1913.

influence which is often sufficient to limit the explosive crises to the hours immediately following midnight and midday. At Kilauea, however, there is normally no actual external eruption in the Italian sense of the word ; the ordinary barometric variations are unimportant, while the quantity of gas emitted is often very difficult to gauge correctly, many of the vapors being transparent and that of water—which is present—being absorbed by the atmosphere in the heat from the glowing lake and generally dissipated without subsequent condensation. In three months of observation the writer was unable to trace any indisputable coincidence between the activities of the lava lake and the curves of a barograph installed on the spot. There exists, nevertheless, a well-defined conviction among the residents to the effect that there is greater activity at or after midnight, and for this there must be some foundation.

But the most powerful of all the forms of external influence upon the height and activity of the lava-column is undoubtedly that of the luni-solar gravitational combinations. Whatever may be the precise mode of action—and the subject cannot be entered upon here—the writer's continued observation of strong eruptive conditions at Vesuvius in 1905 and 1906 ; at Stromboli in 1907 ; Etna 1908 ; Teneriffe 1909 ; Etna 1910 ; Kilauea 1911, and Stromboli in 1912, has convinced him that few facts in volcanology rest upon a firmer basis, providing it is recognized, not as a *cause* of the volcanic activity, but as a force exerting a certain control over the *times* of its maximum manifestations. Once an eruption is begun—and this influence is often effective also in *initiating* the external activity—the eruptive crises almost infallibly coincide with the dates of the luni-solar combinations. The practical advantage to the volcanologist of this knowledge is enormous, enabling him to plan his campaign in advance, to be ready to make the best of the opportunities afforded by the crises ; to employ the intervening periods of minor activity in investigation of the more dangerous localities ; to determine with greater precision the end of the eruption, etc.

In the case of Kilauea not only were the principal interruptions and reversals in the course of the subsidence coincident with the luni-solar combinations, as shown by the curve, but the greater fact of the high lava period coinciding with an especially favorable series of planetary positions in the early summer, was foreseen a year previous to the time, and the writer's visit to the island planned accordingly.

The effects upon the crater basin of so considerable a subsidence of the lava could not fail to be remarkable, and these consisted chiefly of a general downfall of the more recent formations, including virtually the entire mass of the black ledge. At the commencement of the subsidence, the lava lake sank below its shore, as shown in fig. 2, leaving a pit which, it is interesting to remember, stood within the pit walls of the black ledge; this, in turn, being encircled by the walls of Halemaumau, which, itself, lies within the great Kilauea basin, thus forming a series of four pit-like depressions, one within the other. But the shore—undercut and plastic in its foundations—soon yielded to gravity as the support of the lava column was withdrawn, and settled with a downward inclination toward the edge of the lake, as depicted in fig. 3, whereupon the unsupported black ledge began to give way in a series of majestic downfalls, the impressiveness of which cannot be adequately described. Although on a smaller scale, the collapse of these previous formations was comparable to that of Vesuvius after the eruption of 1906.* At the west and north sides the rock of the wall was under a powerful stress and detachment was accompanied by a sharp report as, with a crashing roar, the avalanche of broken rock descended in a cloud of stony dust (fig. 4) to form the talus, which finally extended to the edge of the lake, as may be seen in fig. 3.

Fig. 2.

Fig. 2. The lava sinking in the central pit. Debris of falling walls seen in background.

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* Frank A. Perret: "Vesuvius: Characteristics and Phenomena of the present Repose Period," this Journal, November, 1909.

Fig. 3.

Fig. 3. The banks inclining downward to the level of the lava. Talus of debris from fallen walls reaching to the edge of the lake.

Fig. 4.

Fig. 4. Descent of an avalanche from the north black ledge.

At the east ledge, on the contrary, detachment was gradual, the dislocated masses of rock sliding downward with a long-drawn roll of thunder, making it easy to know, when lying in bed at the station, from which side of the pit an avalanche was descending. Fig. 5 shows the progressive demolition of the east ledge, and the reader should note in the lower view that, not only the detached block, but the entire ledge as well, has settled to a lower level.

Fig. 5.

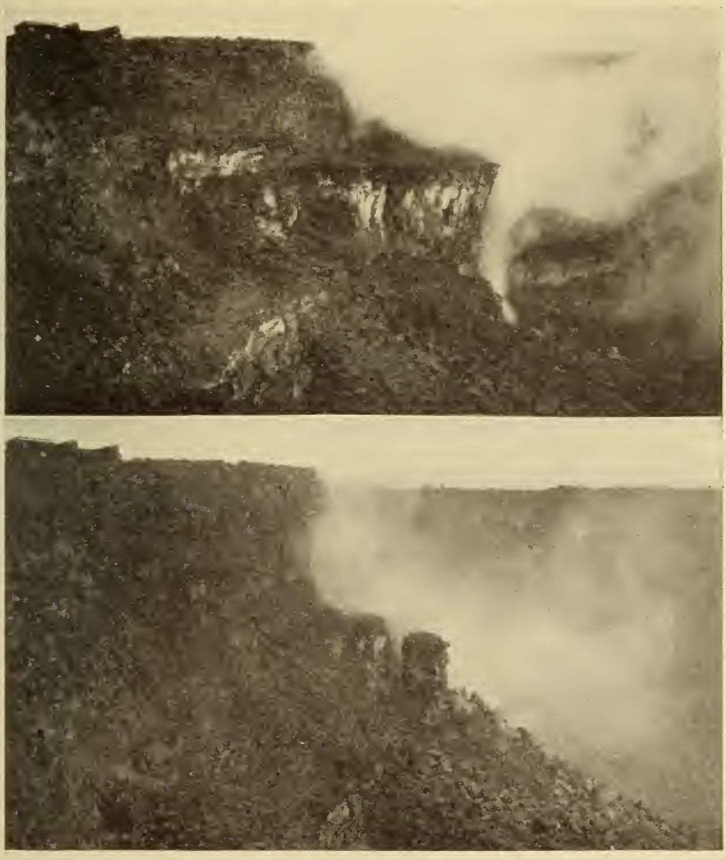

Fig. 5. Showing progressive subsidence and demolition of east black ledge, August 1st and August 24th.

Still more remarkable a phenomenon was the descent of the ledge at the south side of the pit, where the entire mass of solid rock, by a process of almost infinite subdivision, sank with imperceptible motion in a sort of "slow flow" during several weeks of time and presenting the appearance reproduced in fig. 6. The weight of this mass of rock depressed the shore several meters, causing overflows from the lake at this side, in spite of the general lowering of the lava level.

By the end of September the result of this great, though gradual, subsidence of the lava column was a change from the previous pit-like chasm with vertical walls and flat floor, to a cup-shaped cavity formed of debris at the angle of repose, and more nearly resembling the prevailing form of volcanic crater, while the almost total demolition of all recent consolidations left a clean page, so to speak, for the record of a future period of high lava.*

Fig. 6.

Fig. 6. Showing gradual subsidence and "slow flow" of south black ledge. Seen from the west.

The alternating of elevation, with construction by consolidation, and of subsidence, with demolition by collapse, is thus seen to be as characteristic of this as of the other so-called widely variable types of volcanoes—a fact which can but strengthen that increasingly evident bond of fundamental similarity over which so complicated a system of minor and consequent and inevitable variations have been reared.

Posillipo, Naples, February, 1913.

* This was initiated soon after the writer left the islands.

Art. XL.—*Revision of the Genera of Starfishes of the Subfamily Asterininæ*; by A. E. Verrill.

There is, perhaps, no family of starfishes that is so much in need of revision as the Asterinidæ. Even in recent standard works very erroneous statements are made as to the morphology of the group* and the characteristic structures of the genera and subfamilies,† while very diverse species are still included in the old genus *Asterina.* In this brief article I propose to give a summary of the classification of those Asterininæ more nearly allied to *Asterina* proper, and in part usually referred to that genus, but it is not possible to classify all the numerous species at this time. The group is well represented in all the warmer seas, but no species is found on our Atlantic coast‡ north of Florida, except the large and very aberrant species, *Tremaster mirabilis* Ver., often made the type of a separate subfamily. It is from the northern fishing banks. Only one is found on the Pacific coast north of southern California, viz., *Patiria miniata* (Br.).

Subfamily Asterininæ.

Asterinidæ (*pars*) Gray, Ann. and Mag. N. Hist., vi, p. 228, 1840; Synopsis, p. 15, 1866. Perrier, Revis. Stell., iv, p. 291, 1875; v, p. 209, 1876. Viguier, Squellette des Stell., Arch. Zool. Exper., vii, p. 205, pl. xiv, figs. 1–13, 1878 (structure). Sladen, Voy. Challenger, xxx, p. 374, 1889. Perrier, Expl. Trav. et Talism., pp. 141, 163, 1894. Fisher, op. cit., 1911, p. 253 (table of genera).

Body usually rather flat, often thin, sometimes stellate with long rounded rays; usually with five or six short rays, rarely eight. Margins usually thin and formed mainly by the inferomarginals; marginal plates small, usually scarcely larger than the adjacent dorsals, usually with a comb or cluster of spinules. Dorsal plates usually flat and more or less imbricated, sometimes not imbricated; generally covered with minute spinules, often in tufts or combs; sometimes covered with a soft, naked, or granular dermis. Under side flat; actinal plates angular,

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* Thus Gregory, 1900, in Lancaster's Treatise on Zoology, p. 238, erroneously states that the madreporic plate is on the ventral side in *Asterina*, and on page 250 gives as family characters, the absence of pedicellariæ; imbricated plates; and other characters of only generic value.

† Sladen, Voy. Challenger, 1889, p. 374, and Fisher (Asteroidea of N. Pacific, 1911, p. 253), are both in error in stating that the papulæ are generally distributed, and that the dorsal plates do not have descending processes or pillars in Asterininæ, while these characters exist in Anseropodinæ. In fact, the papulæ are always definitely localized, and many typical Asterininæ (e. g. *Patiria*) have strong vertical pillars.

‡ The small specimen formerly described by me, from off the coast of Maine, as *Asterina pymæa*, proves to be the young of a Porania.

flatish, imbricated or closely united, usually covered with small combs or tufts of spinules, sometimes with only one; these plates form regular oblique rows. Adambulacral spines simple, divergent; in two sets; the furrow-spines form small, usually webbed combs of two to eight. Those on the outer surface are in groups or fans, or like the interactinals. Pedicellariæ usually lacking; when present they are two-bladed, erect, forficiform.

The papular pores are dorsal and form several rows on the median and lateral parts of the rays, and sometimes on adjacent parts of the disk, but are absent from the more or less large interradial areas, where the plates assume a different shape and are more closely united.

Fig. 1.

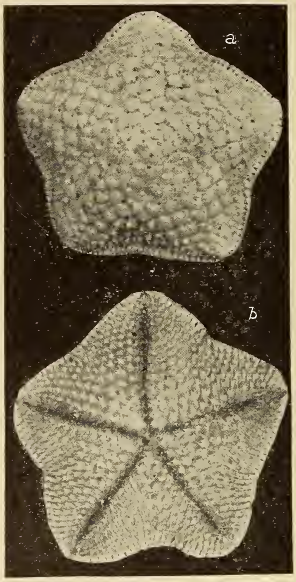

Fig. 1. *Asterinides folium* (Ltk.); *a*, dorsal side; *b*, ventral side, natural size.

There is generally no single dorsal median, radial row of plates; its place is taken by two to four or more alternating rows; the larger of these plates have a papular pore under the proximal edge. These larger plates usually show only one of the edges and part of one side; seen from the inside they appear much larger, often four-lobed, and obliquely imbricated. The dorsal plates of the outer interradial areas, in many species, have conical or pillar-like processes extending downward and meeting similar uprising processes from the outer interactinal plates, as stalactites meet stalagmites*; or they may not join directly, but be united by an intermediate ossicle. In some genera they are differently joined. In typical *Asterina*, and doubtless in many other genera, if not in all, the genital pores are on the ventral side, in a pair, just outside the jaw plates, but they are seldom visible in preserved specimens. The madreporic plate is usually rather large and placed close to the central area of the disk; sometimes there are two or more, rarely five. The rays vary from five to eight, and some species are probably autotomous. The genus *Tremaster* Ver. is remarkable for having an oblong perforation passing entirely through the disk in each interradial area, and for having only one or two furrow-spines.

The following table shows the classification, now proposed, for the principal generic groups:

Table of Genera and Subgenera of Asterininæ.

I. Interradial areas of the disk not perforated.

A. Adambulacral spines form a separate comb or combs within the furrow edge, and another group on outer surface; ventral plates and interspaces not covered by a granulated dermis.

B. Principal dorsal plates are all imbricated.

C. Margins of disk and rays thin, subacute; rays depressed; usually short.

D. Interactinal or ventral plates in regular oblique rows, each with a fan-shaped group of two to eight small spines, usually webbed.

E. Dorsal plates of papular areas nearly all of one kind, the exposed part usually roundish, elliptical, cordate, or shield-shaped, wholly or partly spinulose. Genus *Asterina*, in a wider sense.

a. Two-bladed pedicellariæ occur on the dorsal plates and intervening dermis.

Asterina (restr.) Nardo. Type, *A. minuta* Nardo = *A. gibbosa* (Pen.) = *verruculata* (Retz.) = *A. pulchella* Per. Europe.

aa. No pedicellariæ present.

Asterinides Ver., genus nov. Type, *A. folium* (Ltk.). W. Indies; see fig. 1, Bermuda; Florida.

EE. Dorsal plates of papular areas of two or more diverse kinds, the larger proximally arched or lunate, and notched for passage of papulæ; between these are groups of small ovate or pyriform ossicles inserted endwise, mostly bearing small roundish clusters of spinules. Internal vertical pillars present in interradial areas.

x. No pedicellariæ found.

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* This feature has been regarded hitherto as peculiar to Anseropodinæ, but it occurs also in several genera of Asterininæ, perhaps in all with thin stiff margins.

Patiria Gray, 1840 (monotypic). Type, *P. coccinea* Gray. Cape Good Hope ; E. Africa (not *Patiria* Per. nor of Sladen).

b. Ventral plates have a large solitary spine, or sometimes two. Dorsal plates nearly as in *Patiria*, but with fewer small ossicles.

Patiriella Ver., gen. nov. Type, *P. regularis* Ver. New Zealand ; Australia, etc.

bb. Ventral plates have a fascicle of slender spines.

Asterinopsis Ver., gen. nov. Type, *A. penicillaris* (Lam.). Red Sea ; E. Indies ; Japan ; Australia. *A. pilosa* (Per.), off Dominica I. ; *A. lymani* (Per.), off Barbados.

xx. Two-bladed pedicellariæ on dorsal plates.

Enoplopatiria Ver., nov. Type, *E. marginata* (Hupé)=*A. stellifera* (Mob.)=*A. braziliensis* Ltk.=*A. minuta* (M. & Tr., *non* L.). Brazil ; W. Indies ; Canary Is. ; W. Africa.

CC. Margin of disk and rays not thin ; rays elongated and rounded ; dorsal plates imbricated and spinulated.

c. Adambulacral plates have two or more fan-like rows of superimposed webbed spines on the furrow margin, and an outer group of many spinules. Ventral plates covered with numerous small spinules ; principal dorsal plates imbricated, lunate, finely spinulated, with a small one proximal to papular pore.

Nepanthia Gray. Type, *N. maculata* Gray. E. Indies. Includes, also, *N. brevis* Per. E. Indies, etc.

cc. Adambulacral plates with a single inner comb and an outer fan of spines. Ventral plates with a central roundish cluster of many spines. Dorsal plates nearly as in *Patiria ;* with many interposed small ossicles.

Callopatiria Ver., gen. nov. Type, *C. bellula* Sladen, as *Patiria.* Cape Good Hope. *C. obtusa* (Gray, *non* Ver.). Panama.

BB. Principal dorsal plates are not all imbricated.

F. Rays elongated and rounded.

d. Principal dorsal plates contiguous ; notably enlarged, rounded or elliptical, with a central group of spinules and marginal series of pedicellariæ. Ventral plates with a fan of several spines.

Allopatiria Ver., gen. nov. Type, *A. ocellifera* (Gray), as *Patiria.* Australia.

dd. Principal dorsal plates not greatly enlarged, roundish, separated by small, roundish ossicles around papulæ ; all spinulated. Ventral plates crowdedly spinulated.

Parasterina Fisher. Type, *P. crassa* (Gray), as *Patiria*. Australia. *P. obesa* Clark. Chili; Peru.

FF. Rays not elongated and rounded.

G. Dorsal plates of papular areas roundish, separated by naked skin, having papular pores. Ventral plates with one or two simple spines.

Disasterina Per. Type, *D. abnormalis* Per. New Caledonia; also, *D. ceylonica* Dod. Ceylon.

GG. Dorsal plates of rays thin, contiguous, not overlapping, linear or narrow, transversely elongated, often bent, with many small interpolated ossicles, all covered with even granules. Internally the plates are supported on an alveolar structure. Ventral plates thin, each with a cluster of webbed spines, those adcentral having about four to six in an irregular group; admarginal ones with about three small ones in a comb. Adambulacral furrow spines in convex webbed fans of four or five.

Desmopatiria Ver., gen. nov. Type, *D. flexilis*, nov. Chili?

AA. Adambulacral spines form a continuous webbed series, the individual combs of three to five being united together; no spinules on outer surface. Dorsal and ventral plates and interstices covered with a finely granulated dermis, which also forms the web between the minute spines, in a fan, on the ventral plates. No dorsal spinules. Papular pores form six or more rows. Internal dorso-ventral columns are present near margins. Form depressed pentagonal, with thin margins. A few small ossicles between dorsal plates, usually one.

Stegnaster Sladen. Type, *S. wesseli* Per. Florida; Bahamas; W. Indies; Colon. *S. inflatus* Hutton. New Zealand.

II. Interradial areas of disk perforated vertically. Form large, pentagonal, with the thick disk arched upward and the margins thin; concave beneath. Dorsal plates strong, convex, imbricated, larger papulary ones with spinules on the edge; others with granules. Papular areas radial, petaloid, with numerous papulæ. Ventral plates with one or two flat spines; outer surface of adambulacrals with two; inner margin usually with one spine.

Tremaster Ver. Type, *T. mirablis* V. Newfoundland Banks.

ASTERINA Nardo (restricted).

Asterina NARDO, Oken's Isis, p. 716, 1834. Gray (*pars*), Ann. and Mag. Nat. Hist., vi, p. 286, 1840; Synopsis, p. 16, 1866. Perrier, Revis. Stell., Arch. Zool. Exper. et Gen., v, p. 214, 1876. A. Agassiz, North American Starfishes, p. 106, pl. XIV, 1877 (structure). Viguier, op. cit., vii, p. 207, pl. XIV, figs. 8–13, 1878 (structure). Sladen (*pars*). Voy. Challenger, xxx, p. 388, 1889. Fisher (*pars*), op. cit., 1911*b*, p. 254.

Asteriscus (*pars*) MÜLLER and TROSCHEL, 1840, p. 104; Syst. Aster., p. 39, 1842.

The type of this genus is undoubtedly the common Mediterranean species, *A. gibbosa* (Pen.) = *minuta* Nardo. The genus, as here restricted, has the larger dorsal plates closely imbricated, convex, relatively large and wide, notched on the proximal side; when seen from the inside they are rather rhombic or quadrate and only slightly lobed. There is often a single small, rounded ossicle between them, but no large clusters. The dorsal interradial plates near the margin have stout, conical, descending processes internally. The dorsal radial plates usually have one or two rows of spinules on the edge, and also bear pedicellariæ about as large as the spinules. There may be as many as twelve rows of papulæ. The genital pores are on the ventral side, in pairs, near the jaws. The restricted genus includes, among others, the following:

A. trochiscus (M. & Tr.). E. Indies.

Asterinides Ver., nov.

Includes, besides the type, the following and several others:

A. burtoni (Gray) = *A. cepheus* (M. & Tr.). S. Africa to Red Sea; Ceylon; E. Indies; Philippines; New Guinea, etc.
A. wega (Per.). Has six to eight rays. Red Sea; Mauritius.
A. minuta (Linn., *ex* Gray), *non* M. and Tr. Antilles. Perhaps = *A. folium.*
A. modesta Ver. Panama; Pearl Is.

Patiria Gray, 1840. Type, *P. coccinea* Gray.

This genus includes, among others, the following, besides the type:

P. miniata (Br.). California to Alaska.
P. chilensis (Ltk.). Paita, Peru, to Chili.
P. gayi (Per.). Chili.
P. granulosa Per. Hawaiian Is.
P. pectinifera (M. & Tr.) Japan.
P. granifera (Gray). Cape Good Hope.
P. novæzelandiæ (Per.). New Zealand.

Patiria miniata (Br.) Verrill.

Asterias miniata Brandt, Prodromus, p. 68, 1835.
Patiria miniata Verrill, Trans. Conn. Acad., i, pp. 234, 236, 1867 (distribution).
Asterina miniata Sladen, op. cit., p. 774, 1889. Verrill, American Naturalist, xliii, p. 547, fig. 2 (six-rayed), September, 1909. Fisher, Aster. N. Pacific, p. 254, pl. lvi, figs. 6, 8; pl. lxi, figs. 1-4; pl. lxii, figs. 1, 2, 1911.

This large and variously colored species is common at low-tide and in shallow water from California to southern Alaska.

Though normally five-rayed, six-rayed and seven-rayed examples often occur. It is a typical *Patiria*, closely allied to the type. It has been well described and illustrated recently by Professor Fisher. The following remarks are intended chiefly to illustrate the generic characters.

The larger plates of the papular areas, when the spinules are removed, have the admedian edge prominent, lunate, concave beneath, for the papular pores, and having, on the convex upper side, a raised lunate ridge or crest, which carries the spinules. The small interpolated ossicles form clusters, often of ten to fifteen or more, and on the central area of the disk, often of twenty or more. They are mostly ovate or pyriform with the smaller end inserted into the dermis-like pegs. They do not show on the interior surface. Near the end of the ray, beyond the papulæ, the plates are small, roundish or pelecoidal, with an evenly convex surface. When well preserved or living the plates are covered by a rather thick canaliculated dermis.

The papulæ form ten to twelve radial rows, or even more in large specimens, and extend over the inner part of the interradial areas and center of the disk.

Seen from the inside, the larger radial plates of papular areas are stout, mostly four-lobed, with the two rounded abmedian lobes underlapping two adjacent plates; and the two admedian lobes overlapping the lobes of two plates, with a large papular pore between the lobes. The plates that form the two median rows are obliquely placed, long-ovate, curved, not lobed internally, but with the smaller ends crossed over the median line.

Beyond the papular areas, in the interradial areas, the dorsal plates have a descending conical process, becoming longer on the plates nearer the margin, and united to the ventral plates by a similar process from the latter, or by an interpolated ossicle.

Patiriella Ver., nov. Type, *P. regularis* Ver.

The type has two furrow-spines, sometimes three adorally, and one on the outer surface; these are rather large, tapered, acute, not webbed; spines of the ventral plates are similar, usually solitary. The ventral plates form numerous oblique rows, about fifteen in the longer rows; adoral ones are large and thick, the exposed part three-lobed or shield-shaped, sometimes four-lobed; innermost odd one larger, bilobed, or subcordate; distal ones lancet-shaped; jaw-plates large and thick, angular, prominent; comb of spines about five on each side, stout, blunt.

The larger dorsal radial plates are prominent, arched or lunate, strongly concave and notched beneath, for exit of papulæ; on the summit there is a single or double curved row of small spinules. A few small, rounded ossicles, with similar spinules, are interpolated, usually one or two to a papular pore, but none in the interradial areas, beyond the papular region, where the plates become rounded or shield-shaped and bear a small cluster of spinules.

The inferomarginal plates are small and irregularly placed, smaller and less prominent than the upper ones. Papular pores form about twelve rows.

To this genus, besides the type, belong the following species:

P. exigua (Lam.) = *A. pentagonus* (M. & Tr.); = *A. kraussii* (Gray). Cape Good Hope; East Indies.
P. calcar (Lam.). Australia.
P. fimbriata (Per.). Bourbon I.; Magellan Str.
P. squamata (Per.). Senegal.
P. calcarata (Per.). Chili.
P. pusilla (Per.). Chili.
P. gunnii (Gray). New Zealand; Australia.

Desmopatiria Ver., gen. nov.

This very peculiar starfish, of which the principal generic characters are given in the table, p. 481, is remarkable for the peculiar alveolar structure underlying the plates, above and below, and in the interradial areas extending from the dorsal to the ventral plates, as tubes. It is possible that in life they contained calcareous deposits that have been dissolved by the acidity of weak alcohol, for the ventral spinules appear corroded in many places.

Aside from this structure the dorsal skeleton is peculiar in having very numerous linear plates, with smaller, roundish, closely granulated flat plates, not overlapping nor imbricated; and in the irregular clusters of webbed spines on the ventral plates.

The dry specimen has the disk swollen and distorted and the rays strongly curved upward, showing unusual flexibility in life.

Desmopatiria flexilis Ver., sp. nov.

Form stellate, with five short, broad rays. Disk swollen, in the central and radial areas; margins thin, with small marginal plates, about the size of adjacent dorsals and closely granulated in the same way; the lower ones are the more prominent. Radii, 17^{mm} and 26^{mm}; ratio, 1:1·53; elevation in middle of disk, 15^{mm} when dry.

The larger dorsal plates of the wide radial areas are narrow, transversely elongated, often in transverse series, partly nearly straight, but often bent, closely crowded together but not overlapping, and with narrow grooves between them. Between these are many much smaller ones, of varying form and size, mostly rounded or elliptical. All the dorsal plates are entirely and evenly covered with crowded, minute granules, or granule-like blunt spinules. The plates in the interradial areas become more regular, polygonal or roundish, closely compacted, thin, and rest on the summits of polygonal tubes, having a honeycomb-like appearance, in miniature, when the plates are removed. On the radial and central areas, and also on the ventral side, there is a short tube or cell under each plate, limited below by the underlying thin membrane, producing an alveolate structure.

Papulæ are small and stand singly, in several ill-defined radial rows.

The adambulacral spines form a strongly webbed fan of three or four unequal spines on each plate, and an outer rounded cluster of four or five rather stout spinules, webbed together. The ventral plates, toward the center, have an irregular group of three to six webbed spines; toward the margin these become more regular and finally form transverse combs of about three on each plate. Jaw-spines form a regular rounded comb of about six on each side, webbed together.

Locality uncertain; received in a lot containing Chilian starfishes, such as *Heliaster helianthus*, and *Meyenaster** *gelatinosus* (Meyen) Ver., but without a label. (Mus. of Yale Univ.; one, dry.)

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* *Meyenaster* is proposed as a new genus, with this species as the type. It is monacanthid; has one interactinal row of plates, and a reticulated dorsal skeleton, with numerous papular areas and one or three rows of stout spines. The type is six-rayed; another species is five-rayed.

ART. XLI.—*On the Hydrolysis of Esters of Substituted Aliphatic Acids*; by W. A. DRUSHEL and E. W. DEAN.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxliv.]

5. ETHYL ESTERS OF LACTIC ACID, GLYCERIC ACID, α-ETHYLOXY AND β-ETHYLOXY PROPIONIC ACIDS.

Preliminary Discussion.

IN a preceding paper* we announced our intention of continuing a study of the effect of substituted hydroxyl groups on the velocity of hydrolysis in acid solution. The substance first studied in this connection was ethyl glycollate, which was found to react somewhat more rapidly than ethyl acetate. Three alkyloxy acetates were also studied, and here a retardation was found to occur. This effect increases with the size of the substituted group, but the difference is less between the last two than between the first two members of the series.

The esters we proposed to consider next were the alpha hydroxy propionate (lactate), the beta hydroxy propionate (hydracrylate), and the alpha, beta, dihydroxy ester (glycerate). After a considerable amount of work we have as yet been unable to discover any practical method of preparing pure ethyl hydracrylate in sufficient quantity for our use. Experiments toward that end are still in progress and we hope to be able to give an account of them in a future paper. We have, however, been able to obtain some information as to the relative effect of alpha and beta positions of a substituted radical by the determination of the velocity constants of the two ethyloxy propionates.

Preparation of the Esters.

Ethyl lactate was obtained from The Hoffman & Kropff Chemical Co. The ester was purified by fractional distillation and a portion obtained for use which boiled at from 154·5° to 155°.

The preparation of ethyl glycerate was carried on as follows: Calcium glycerate was obtained by oxidizing glycerine with nitric acid in tubes,† neutralizing with calcium carbonate and recrystallizing to purify the product. The acid was obtained by precipitating the calcium with the theoretical amount of oxalic acid, filtering and evaporating to dryness by keeping for several days on the steam bath. From this the ester was obtained by Frankland and McGregor's‡ modification of the method of Henry.§ The

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* This Journal, xxxiv, 293.

† Mulder, Ber., ix, 1902.

‡ Proc. Chem. Soc., lxiii, 512.

§ Ber., iv, 706.

dry glyceric acid was sealed in a tube with three to four volumes of absolute alcohol in the absence of any catalyzing agent and heated for about four hours at a temperature of 180° to 190°. The excess of alcohol was then distilled off on a water bath and the ester purified by fractioning under diminished pressure. The product obtained boiled at a constant temperature of about 130° at about 20^{mm} pressure, which corresponds fairly well with the figures given by Frankland and McGregor; —120° to 121° at 14^{mm}. The ester boils under atmospheric pressure in the neighborhood of 230°, but at this temperature a certain amount of decomposition takes place which is entirely avoided by the reduction of pressure.

The alkyloxy esters were obtained by the general method described in the previous paper.* The reactions are: for the alpha ethyloxy propionate,—

$$CH_3CHCl.COOC_2H_5 + NaOC_2H_5 \\ = CH_3CH.OC_2H_5.COOC_2H_5 + NaCl,$$

and similarly for the beta product. The alpha ester boils at 154·5° to 155·5° and the beta ester at 166°.

Ethyl lactate and ethyl glycerate are easily soluble, as is to be expected from the fact that they contain hydroxyl groups. The alkyloxy esters appear to be rather difficultly soluble.

Procedure.

The experiments were carried out in the thermostat described in the first paper† of this series. The esters were hydrolyzed in 250^{cm^3} flasks which were filled to the mark with decinormal hydrochloric acid and warmed to the temperature of the thermostat before starting the reaction. The esters were measured out in quantities of about $2·5^{cm^3}$ from a graduated pipette. At regular intervals 25^{cm^3} portions were withdrawn from the flasks by means of pipettes, run into cold water and titrated immediately with decinormal barium hydroxide solution. Phenol phthalein was used as an indicator.

Experiments were carried on at temperatures of 25°, 35°, and 45°, duplicate results being obtained in some of the cases. Calculations were made by the use of the well-known titration formula for reactions of the first order.

The esters studied in this series hydrolyze at such different rates that it is inconvenient to tabulate figures giving the time period represented by each constant. Consequently we record simply the time in minutes over which the reaction was measured. This was in all cases sufficient to allow the hydrolysis to proceed at least two-thirds of the way to completion. Values in parentheses are not counted in the averages, it being assumed

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* This Journal, xxxiv, 293.

† Ibid., xxx, 72.

on account of their irregularity that they are unduly influenced by experimental error.

TABLE I.

Hydrolysis at 25°. N/10 HCl

Ester........	Ethyl Propionate	Ethyl Lactate	Ethyl Glycerate	Ethyl Ethyloxy Propionates	
				α	β
Time........	2880	2880	5760	5760	5760
10^5K......	72·1	71·1	19·0	20·3	15·0
	71·4	74·7	18·8	19·6	14·4
	73·2	74·4	18·4	19·6	14·1
	72·3	74·7	18·4	19·8	14·0
	71·7	73·6	18·3	19·9	14·1
	70·9	72·2	18·3	19·9	14·1
	69·8	71·6	18·2	---	---
Averages..	71·6	73·2	18·5	19·7	14·3
Averages.. (duplicate)	72·8	74·4	---	19·6	13·5
Hydrolysis at 35°.					
Time........	1440	1440	4320	5780	5780
10^5K......	181·	178·	44·8	49·3	35·5
	180·	179·	44·2	49·7	35·2
	180·	178·	44·0	49·3	34·9
	178·	178·	43·7	49·2	35·4
	178·	178·	43·1	49·1	35·1
	178·	177·	43·2	50·3	(34·0)
	(173·)	(169·)	43·3	(45·7)	
Averages..	179·	178·	43·9	49·5	35·2
Averages.. (duplicate)	181	180	43·6	---	---
Hydrolysis at 45°.					
Time........	630	630	2190	2190	2190
10^5K......	402·	389·	98·2	109	(77·2)
	416·	399·	101·	112·	83·6
	406·	399·	102·	114·	86·5
	408·	394·	102·	113·	85·9
	402·	400·	102·	110·	84·3
	400·	398·	102·	109·	84·3
	406·	392·	101·	(106)	83·6
Averages..	406·	396·	101·	111·	84·7

TABLE II.—Summary.

Temperature	25° 10^5K	35° 10^5K	45° 10^5K	25°–35° Temp. Coeff.	35–45 Temp. Coeff.
Ethyl propionate	71·6	179·	406	2·50	2·26
Ethyl lactate	73·2	178·	396·	2·43	2·22
Ethyl glycerate	18·5	43·9	101·	2·43	2·20
Ethyl α-ethyloxy propionate	19·7	49·5	111·	2·51	2·24
Ethyl β-ethyloxy propionate	14·3	35·2	84·7	2·45	2·41
Ethyl acetate	64·7	163·	374·	2·51	2·29
Ethyl glycollate	70·4	173	392·	2·45	2·26

Discussion of Results.

The general results brought out by these figures need no extended discussion. There are, however, several points which are evident only on a close examination of the tables. In the first place it will be noticed that the temperature coefficient of the hydroxy esters is low. This is shown in the cases of glycerate, lactate and glycollate. The figures for the last ester are repeated from tables in a previous paper. In the case of lactate and propionate this difference in the temperature coefficient is sufficient to cause the former to hydrolyze more slowly than the latter at 45°, while at 25° its constants are greater. These differences are small, but are nevertheless very clearly marked. The second fact to which attention is called is that ethyl glycerate hydrolyzes very slowly. This means that the presence of hydroxyl groups in alpha and beta positions causes an entirely different effect from that produced by the substitution of a single radical.

From these two facts it would seem that the effect on ester hydrolysis in acid solution cannot be considered as an additive property for all substituted groups. It is here shown that the same group may cause either a slight acceleration or retardation accordingly as the temperature is high or low. It also appears that the presence of two hydroxyl groups may produce a strong decrease of velocity whereas one tends on the whole toward an acceleration.

A single other point is worthy of special mention. An ethyloxy group in the alpha position produces a retardation of the reaction; one in the beta position has a still greater effect. A similar result* was obtained in the cases of the chlor and brom propionates and there is an indication that this may prove to be the general rule. The other results of this paper seem to point toward the absence of general rules governing the behavior of esters hydrolized in acid solution.

Summary.

1. Ethyl lactate has a velocity of hydrolysis in acid solution about two per cent greater than that of the propionate at 25°, practically equal to it at 35° and about two per cent less at 45°.
2. Ethyl glycerate hydrolyzes about one-fourth as fast as ethyl propionate.
3. Ethyl alpha ethyloxy propionate and ethyl beta ethyloxy propionate have velocities respectively about twenty-seven per cent and twenty-one per cent of that of the propionate.
4. Hydroxyl substituted esters seem to have a low temperature coefficient.
5. The beta position of a retarding radical appears to increase its effect.
6. The effect on acid hydrolysis of substituted hydroxyl groups is not an additive property.

Further work has been begun on the reaction velocities of various butyrates. It is intended that this series shall include normal and iso-butyrates, the alpha and beta hydroxy-butyrates and ethyl hydroxy-isobutyrate.

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* This Journal, xxxiv, 69.

Art. XLII.—*The Dispersion of Metals;* by Lynde P. Wheeler, Asst. Prof. of Physics, Sheffield Scientific School of Yale University.

The increase in our experimental knowledge of the dispersion of metals in the past ten years invites a more complete discussion than it thus far seems to have called forth of those relations between the optical and other physical constants of metals which theory demands. The most detailed investigation of these relations which has been made up to the present time appears to be that of Nicholson.* In his paper he uses the equations of the theory to calculate (in the manner first pointed out by Schuster) the ratio of the number of free electrons to the number of molecules in unit volume; and also to the calculation of the values of the so-called dielectric constants of the metals. He discusses, however, only the classical measurements of Drude, and hence the consideration of dispersion was practically excluded. In fact nowhere, to the author's knowledge, has there appeared an adequate discussion of the more modern measurements of Minor,† Bernoulli,‡ Tool,§ Ingersoll,‖ and Tate,¶ in the light of the demands of the electron theory.

As a result of the work of these investigators we possess measures of the optical constants at wave lengths extending in the cases of silver, copper, cobalt and steel from about $\cdot 23\mu$ to $2\cdot 25\mu$; in the case of nickel from $0\cdot 42\mu$ to $2\cdot 25\mu$; and for gold from $0\cdot 4\mu$ to $0\cdot 7\mu$. The values of the indices of refraction (n) and of the coefficients of absorption ($n\kappa$) obtained by these observers for the metals named (with the exception of steel) are brought together in the third and fourth columns of Tables I–V, and are shown graphically in the two lower curves of the corresponding figures I–V. The observations at all of the wave lengths at which measurements were made are not included, but none are omitted except where the trend of the curves is so uniform that many points are unnecessary. The data for steel are omitted because the chemical and physical complexity of this material is such as to render all the physical constants required for a comparison with theory so uncertain as to make such a study fruitless.

A study of these tables or curves reveals two salient facts with regard to the precision of the measurements. First, that the results of different observers at the same wave lengths differ in general by an amount considerably in excess of the errors

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* Nicholson, Phil. Mag. (6), xxi, p. 245, 1911.

† Minor, Ann. Phys., x, p. 581, 1903.

‡ Bernoulli, Ann. Phys., xxix, p. 585, 1909.

§ Tool, Phys. Rev., xxxi, p. 1, 1910.

‖ Ingersoll, Astroph. Jour., xxxii, p. 265, 1910.

¶ Tate, Phys. Rev., xxxiii, p. 321, 1912.

inherent in the methods of measurement employed; and second, that in an equally general manner the different observers are in very close agreement as to the amount and trend of the dispersion. Thus it will be observed that for those regions of the spectrum where the results of the different observers overlap, the curves for both n and $n\kappa$ are in general parallel though not coincident; and also that the departures from parallelism are in the main much less than the discrepancies in the absolute values. In copper alone is there any real disagreement as to the trend of the dispersion. Here the measures of Tool and Tate would locate the minimum in the curve for n farther up in the spectrum than do those of Ingersoll.*

Fig. 1.

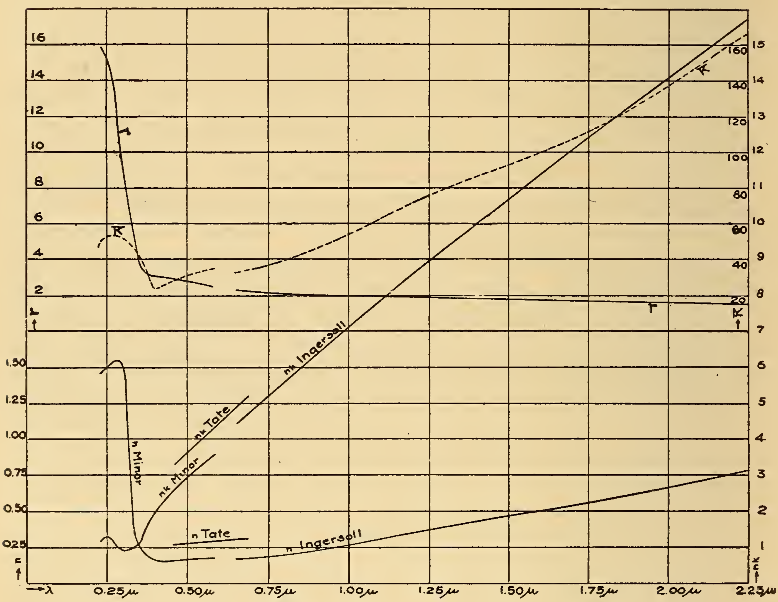

Fig. 1. Silver.

The discrepancies in the values obtained at any given wave length are to be attributed to differences in the state of the reflecting surface. These arise from small differences in the

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* Bernoulli's values for nickel also form an exception to the general parallelism of the dispersion curves. Too much stress cannot be laid on his measures, however, as his experimental method seems to be open to objection. See Voigt, Ann. Phys., xxix, p. 956, 1909.

method or duration of polishing, or possibly (as is suggested by the work of Lummer and Sorge* on glass) they may arise from different states of strain existing in the surface of different samples of the same material. There seems to be, at least tacitly, a general opinion that since Drude's specification of the "normal" condition for a reflecting surface, it only requires sufficient care in the preparation of a metallic mirror in order to get consistent results; and that consequently our knowledge

TABLE I—SILVER.

Observer	λ	n	nk	$\frac{n^2\kappa}{\lambda^3}(10)^{-12}$	r	$n^2(\kappa^2-1)$	A	K
Minor	0·231μ	1·43	1·11	129	15·7	−0·80	46·3	47·1
"	·250	1·49	1·32	125·	15·4	−0·47	51·8	52·3
"	·298	1·56	0·91	53·6	10·1	−1·61	49·5	51·1
"	·346	0·219	1·10	5·80	3·41	+1·16	40·9	39·7
"	·395	0·155	1·91	4·81	3·01	3·64	25·6	22·0
"	·450	0·164	2·39	4·29	2·91	5·67	32·8	27·1
Tate	·460	0·270	3·25	------	----	------	----	----
Minor	·550	0·169	2·94	3·97	2·74	8·63	38·1	29·5
Tate	·500	0·273	3·56	------	---	------	----	----
Minor	·500	0·176	3·31	3·50	2·57	10·9	43·4	32·5
Tate	·580	0·284	4·20	------	----	------	----	----
Drude	·589	0·181	3·67	------	----	------	----	----
Minor	·589	0·177	3·64	3·15	2·44	13·2	47·0	33·8
Tate	·620	0·291	4·52	------	----	------	----	---
Drude	·630	0·203	3·96	------	---	------	----	---
Ingersoll	·65	0·154	4·34	2·43	2·14	18·8	50·1	31·3
Tate	·660	0·299	4·87	------	----	------	----	---
"	·700	0·308	5·20	------	----	------	----	---
Ingersoll	·87	0·203	6·07	1·88	1·89	36·8	79·1	42·3
"	1·25	0·37	8·88	1·69	1·77	78·6	152·	73·4
"	1·75	0·55	12·3	1·27	1·55	151·	260·	109·
"	2·25	0·77	15·4	1·04	1·41	230·	394·	164·

of the optical constants is nearly as precise as that of the methods of measurement used. It is safe to say, however, that no one who has had much experience in this line of work has held such an opinion for long. In fact, experience teaches that it is well nigh impossible to exactly reproduce (even by the same observer) the same condition of the reflecting surface in different samples of the identical material, or even in the same sample at different times. Thus we cannot regard the experimental values of the optical constants of metals as anything but rather rough approximations to the specific values characteristic of the substances. Hence any theoretical relation dependent for its numerical evaluation on the absolute values

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* Lummer and Sorge, Ann. Phys., xxxi, p. 325, 1910.

of the optical constants is incapable of yielding dependable results.

On the other hand, since, as has been pointed out above, the data at our command as to the *relative* values of the optical constants at different wave lengths are in general of a higher order of precision, it would seem that a comparison of these results with the dispersion formulæ yielded by the electron theory should yield results of some value. To make such a comparison is the object of this paper.

Fig. 2.

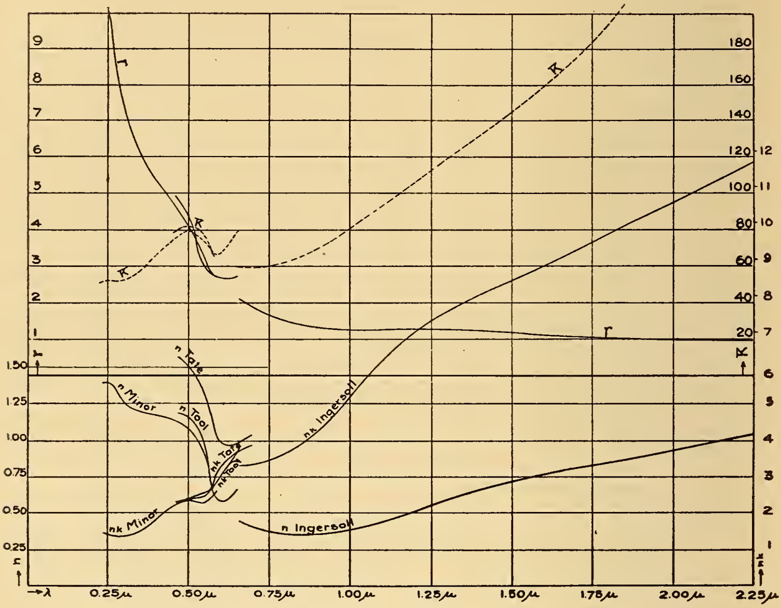

Fig. 2. Copper.

It may be mentioned in passing that it would seem to be possible to obtain accurate absolute values really representing specific properties of the substance in the case of mercury; for the author* has shown that in the case of this metal it is possible to reproduce exactly, surface conditions entirely free from all films of impurity. The possibility of different states of surface strain at different times would also, of course, be eliminated. Work on the dispersion of mercury is now under way in order

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* Wheeler, Phil. Mag., xxxi, p. 229; also this Journal, xxxii, p. 85, 1911.

to obtain with this more promising material data which will enable us to make a more satisfactory comparison with theory than is possible with other substances.

With regard to the properties of the metals revealed by the data under discussion, it will be observed that all five of the substances show in general a decrease of the absorption coefficient (increase in transparency) with increasing frequency of the incident light. In the cases of silver and gold and, with less certainty, copper, there is a minimum in the curve followed by a feeble maximum further up in the spectrum. Thus for silver there is a distinct "transmission" band in the ultra-violet with its center at about 0·316μ; for gold, a less distinct one in the visible spectrum central at about 0·480μ; while for copper there are apparently two minima of absorption, one in

Table II—Copper.

Observer	λ	n	nk	$\frac{n^2\kappa}{\lambda^3}(10)^{-12}$	r	$n^2(\kappa^2-1)$	A	K
Minor	0·231μ	1·39	1·46	163·	11·8	0·19	50·0	49·8
"	·257	1·40	1·42	117·	9·96	0·06	52·1	52·0
"	·298	1·26	1·32	62·7	7·31	0·16	51·5	51·3
"	·347	1·19	1·47	41·8	5·97	0·73	56·7	56·0
"	·395	1·17	1·76	33·4	5·34	1·73	66·1	64·4
"	·450	1·13	2·15	26·6	4·77	3·34	76·6	73·3
Tate......	·460	1·57	2·26	------	----	------	----	----
Tool......	·460	1·19	2·29	27·9	4·89	3·72	82·4	78·7
"	·500	1·17	2·38	22·2	4·37	4·30	86·9	82·6
Tate......	·500	1·50	2·37	------	----	------	----	----
Minor	·500	1·10	2·34	20·6	4·19	4·24	83·2	79·0
Tate......	·540	1·38	2·46	------	----	------	----	----
Tool......	·540	1·07	2·41	16·4	3·13	4·66	84·1	79·4
Minor	·550	0·892	2·23	12·0	3·20	4·18	77·0	72·8
Tool......	·560	0·855	2·42	------	----	------	----	----
Tate......	·580	1·07	2·84	------	----	------	----	----
Tool......	·580	0·600	2·79	8·60	2·71	7·44	72·4	65·0
Drude	·589	0·641	2·62	------	----	------	----	----
Minor	·589	0·617	2·63	7·90	2·60	6·52	71·6	65·1
Tate......	·600	0·980	3·19	------	----	------	----	----
Tool......	·620	0·580	3·32	8·10	2·63	10·9	80·4	69·5
Drude	·630	0·580	3·04	------	----	------	----	----
Tool......	·640	0·615	3·58	8·40	2·68	12·4	87·5	75·1
Tate......	·640	0·958	3·53	------	----	------	----	----
Ingersoll..	·65	0·44	3·26	5·21	2·10	10·4	70·5	60·1
Tool......	·660	0·655	3·78	8·64	2·72	13·9	94·1	80·2
Tate......	·660	0·996	3·70	------	----	------	----	----
"	·700	1·035	3·82	------	----	------	----	----
Ingersoll .	·87	0·35	3·85	2·05	1·32	14·7	79·4	64·7
" .	1·25	0·56	7·28	2·09	1·33	52·7	165·	113·
" .	1·75	0·83	9·46	1·47	1·12	90·7	273·	182·
" .	2·25	1·03	11·7	1·06	1·02	136·	420·	284·

the ultra-violet at about 0·3μ, and the other in the visible spectrum at about 0·55μ. In the cases of nickel and cobalt the minima in the absorption curves (if they exist) have not been reached within the limits of the spectrum over which these observations extend; both of these metals show a more or less steady decrease in $n\kappa$ throughout the whole range, though in the case of cobalt a minimum seems to be indicated not far beyond the range of the observations in the ultra-violet. It is to be noted further that the reflection coefficient (not shown in tables or figures) shows a minimum value at the same points in the spectrum as does $n\kappa$.

Fig. 3.

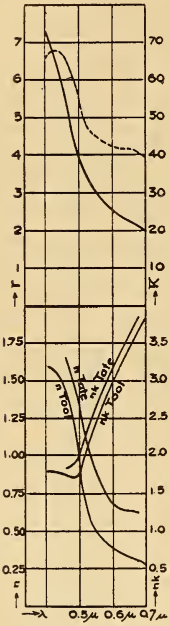

Fig. 3. Gold.

The indices of refraction also show marked minima in the cases of the three better conductors. That for silver occurs at 0·395μ; that for copper at about 0·62μ (Ingersoll's results would place it beyond 0·7μ); and that for gold is apparently located just beyond the longest wave length for which we have measurements (0·7μ). For nickel and cobalt there are no such marked minima; the curves show an index decreasing tolerably uniformly with increasing frequency throughout the range over which the experiments extend. A minimum in the case of cobalt seems imminent, however, just beyond that range. For a large range of the spectrum the numerical value of the index is, in the case of the three better conductors, less than unity; while for the other two it is approaching such a value in the ultra-violet. The fact that the index of refraction is less than unity for silver and gold and copper in the visible spectrum has been verified, it may be remarked, by the direct measurement of the deviation produced by prisms of very acute angle.

The theoretical relations which it is proposed to discuss are those yielded by the well-known equation of condition for the propagation of waves in a medium possessing both conductivity and a dielectric constant

$$\nabla\cdot\nabla E = \frac{K}{C^2}\ddot{E}\,4 + \pi\sigma\dot{E},$$

where E is the electric force, σ the conductivity, K the dielectric constant, C the velocity of light (which enters owing to the use of electro-magnetic units), and $\nabla\cdot\nabla$ is the Laplacian

TABLE III—GOLD.

Observer	λ	n	nk	$\frac{n^2\kappa}{\lambda^3}(10)^{-12}$	r	$n^2(\kappa^2-1)$	A	K
Tool......	0·400μ	1·58	1·79	44·2	7·49	0·71	66·5	65·8
"	·420	1·57	1·80	38·2	6·97	0·78	67·9	67·1
"	·440	1·55	1·79	32·4	6·40	0·83	68·6	67·8
"	·460	1·45	1·74	25·7	5·70	0·93	67·0	66·1
Tate......	·460	1·66	1·83	------	----	------	----	----
Tool......	·480	1·28	1·69	19·6	4·96	1·21	63·3	62·1
Tate......	·480	1·53	1·87	------	----	------	----	--
Tool......	·500	0·935	1·75	13·1	4·07	2·19	58·3	56·1
Tate......	·500	1·33	2·01	------	--	------	----	----
Tool......	·520	0·670	2·01	9·55	3·47	3·60	51·7	47·9
Tate......	·520	1·10	2·19	------	--	------	----	----
Tool......	·540	0·535	2·31	7·83	3·15	5·02	51·3	46·3
Tate......	·540	0·937	2·55	------	----	------	----	----
Tool......	·580	0·415	2·75	5·85	2·72	7·40	50·9	43·5
Tate......	·580	0·729	3·02	------	----	------	----	----
Drude	·589	0·366	2·82	------	----	------	----	----
Tate......	·600	0·666	3·24	------	----	------	----	----
Tool......	·620	0·350	3·16	4·64	2·42	9·88	51·8	41·9
Tate......	·620	0·645	3·41	------	----	------	----	----
Drude	·630	0·306	3·12	------	----	------	----	----
Tool......	·660	0·320	3·54	3·94	2·23	12·4	54·1	41·7
Tate......	·660	0·636	3·73	------	----	------	----	----
"	·680	0·617	3·86	------	----	------	----	----
Tool......	·700	0·280	3·80	3·10	1·97	14·3	53·8	39·5

operator. A transverse wave-train advancing in the x direction with a velocity V may be specified by

$$E_y = E_0 e^{ip\left(\frac{x}{V} - t\right)},$$

where p is the frequency and $i = \sqrt{-1}$. With the aid of this, the equation of condition becomes

$$\frac{C^2}{V^2} = K + i\frac{4\pi C^2\sigma}{p},$$

Since the real part of the ratio C/V is by definition the index of refraction (n), we set $C/V = n(1+i\kappa)$,* and hence we have

$$n^2(1 - \kappa^2 + 2i\kappa) = K + i\frac{4\pi C^2\sigma}{p}. \qquad (1)$$

The significance of $n\kappa$ becomes evident on substituting the value of V in the equation of the wave train, which then becomes

$$E_y = E_0 e^{-\frac{pn\kappa}{C}x} e^{ip\left(\frac{n}{C}x - t\right)}$$

* Drude's notation.

Hence $n\kappa$ is seen to be of the nature of an extinction or absorption coefficient.

Now in equation (1) it is to be observed that the values of K and σ contemplated are those operative for currents of the frequency of those set up by the incident wave-train. If we use the (constant) values for them given by experiments with

Fig. 4.

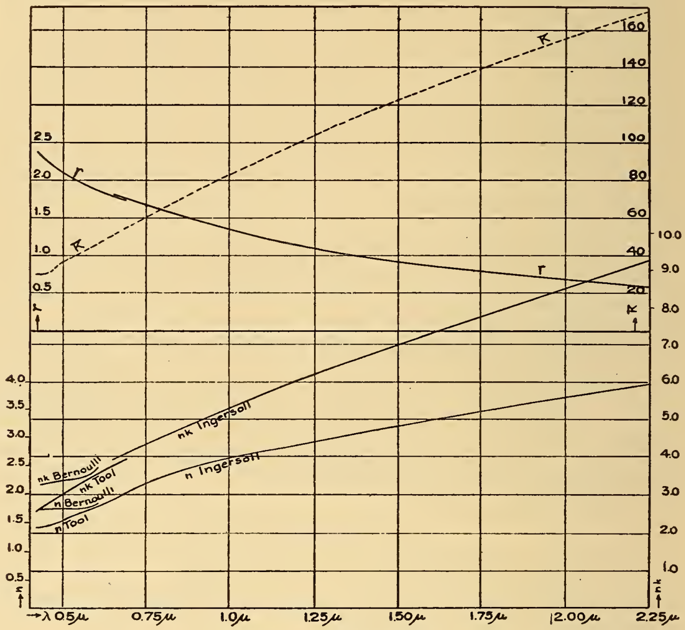

Fig. 4. Nickel.

steady currents, the equation yields, on equating the imaginary and real terms of each side

$$n^2\kappa = \frac{2\pi C^2\sigma}{p} \quad \text{and} \quad n^2(1-\kappa^2) = K \ ,$$

relations, which as has been many times pointed out, are far from being experimentally confirmed. And in view of the enormous frequency of the currents which accompany light waves, it is not surprising that such discrepancies should present themselves. If, however, K and σ can be expressed as functions of the frequency, then equation (1) will yield dispersion formulæ with which the results of experiment can be compared. Such expressions for K and σ have been obtained by several investigators proceeding from the general hypotheses of the electron theory. The formulæ thus obtained for K involve, however, too many undetermined constants to allow of a satisfactory evaluation with the experimental data at our command. Hence it seems best for the present purpose to leave K indeterminate in the equations. The expressions which have been obtained for σ, on the other hand, contain but one undetermined constant and consequently can be profitably used.

TABLE IV—NICKEL.

Observer	λ	n	nk	$\frac{n^2\kappa}{\lambda^3}(10)^{-12}$	r	$n^2(\kappa^2-1)$	A	K
Tool	0·420μ	1·42	2·53	48·3	2·38	4·40	34·0	29·6
Bernoulli	·436	1·74	3·28	------	----	------	----	----
Tool	·460	1·46	2·75	41·3	2·21	5·44	34·9	29·4
Bernoulli	·492	1·74	3·37	------	----	------	----	----
Tool	·500	1·54	2·98	36·6	2·11	6·47	42·8	36·3
"	·540	1·63	3·20	33·0	1·98	7·50	46·7	39·2
Bernoulli	·546	1·76	3·44	------	----	------	----	----
"	·578	1·75	3·48	------	----	------	----	----
Tool	·580	1·73	3·41	30·2	1·90	8·62	51·3	42·7
Drude	·589	1·79	3·32	------	----	------	----	----
Bernoulli	·615	1·85	3·72	------	----	------	----	----
Tool	·620	1·82	3·61	27·6	1·82	9·74	56·0	46·3
Drude	·630	1·89	3·56	------	----	------	----	----
Ingersoll	·65	1·91	3·93	27·4	1·81	11·8	61·2	49·4
Tool	·660	1·95	3·84	26·0	1·77	11·0	61·8	50·8
"	·700	2·03	3·98	23·5	1·68	11·7	66·2	54·5
Ingersoll	·87	2·45	4·80	17·9	1·48	17·0	88·0	71·0
"	1·25	2·92	6·15	9·22	1·07	29·3	132·	103·
"	1·75	3·45	7·76	5·00	0·79	48·3	188·	140·
"	2·25	3·95	9·20	3·19	0·60	69·2	237·	168·

The development of σ in terms of the frequency of the current is best accomplished by the method due to Lorentz, Jeans, and H. A. Wilson. It seems preferable to that of Drude in that the frictional term in the equation of motion of the free electrons in the latter's method receives a more probable physical interpretation in the more recent method. In this method the equation of motion of the electrons is obtained from a consideration of the loss of momentum (in the direction of the acting electric force) sustained by a group of electrons having velocities lying between v and $v+dv$. If we assume that the electric force is given by $E=E_0e^{-ipt}$, and that the law of the distribution of the velocities among the groups is that of Maxwell, we obtain from a consideration of the rate of production of heat per unit volume

$$\sigma = 2q\sigma_0 \int_0^\infty \frac{(v + i\sqrt{\frac{a}{q}}\, e^{-qv^2} dv)}{(1 + \frac{a}{qv^2})}, \tag{2}$$ *

where q is three-halves of the square of the average electronic velocity, σ_0 is the electrical conductivity for steady currents, and

FIG. 5.

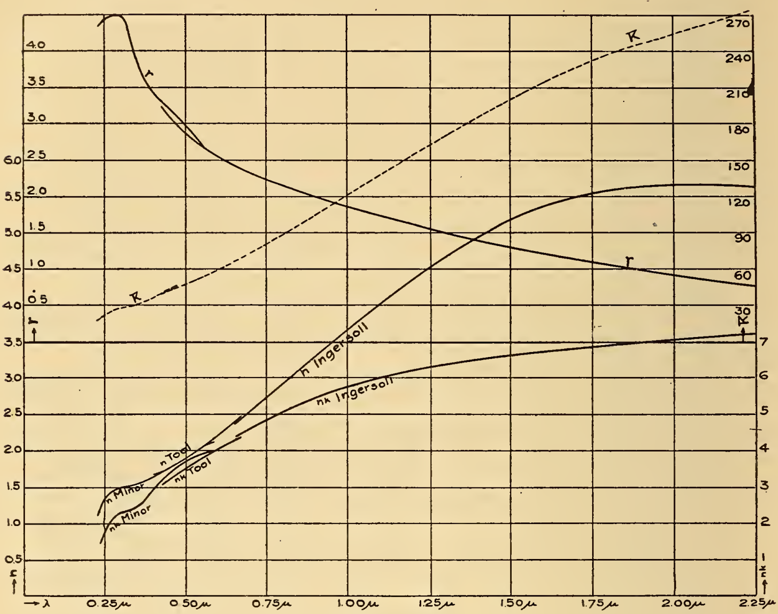

FIG. 5. Cobalt.

$$a = \frac{\pi p^2 m^2 \sigma_0^{\,2}}{4N^2 e^4}, \tag{3}$$

with e the charge, m the mass, and N the number of electrons per unit volume.

If we now expand $(a/qv^2+1)^{-1}$ in series and integrate term by term, we get

$$\sigma = \sigma_0 \left[\frac{1}{a} \left(1 - \frac{2!}{a} + \frac{3!}{a^2} - \cdots\cdot \right) + \frac{i}{2} \sqrt{\frac{\pi}{a}} \left(1 - \frac{1\cdot3}{2a} + \frac{1\cdot3\cdot5}{(2a)^2} - \cdots\cdot \right) \right],$$

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* H. A. Wilson, Phil. Mag. (6), xx, p. 835, 1910. Wilson there assumes the electric force to be given by $E = E_0 \cos pt$, and hence his value for σ lacks the imaginary term of the above.

or,

$$\sigma=\sigma_0\left[\frac{1}{a}\sum_{0}^{\infty}\frac{n!}{a^{n-1}}+\frac{i}{2}\sqrt{\frac{\pi}{a}}\sum_{0}^{\infty}\frac{(2n-1)\ (2n-3)\cdots 1}{(2a)^{n-1}}\right]. \quad (4)$$

These integrations were first performed by Nicholson.* I am unable, however, to confirm his values for the numerical coefficients in the expansions, but find them as given above.

TABLE V—COBALT.

Observer	λ	n	nk	$\frac{n^2\kappa}{\lambda^3}(10)^{-12}$	r	$n^2(\kappa^2-1)$	A	K
Minor	0·231μ	1·10	1·43	127·	4·33	0·83	18·3	17·7
“	·298	1·50	2·33	132·	4·48	3·17	32·0	28·9
“	·347	1·54	2·47	92·0	3·74	3·74	35·2	31·5
“	·395	1·63	2·91	77·1	3·44	5·83	42·0	36·2
Tool......	·420	1·68	3·07	69·6	3·26	6·60	44·9	38·3
Minor	·450	1·79	3·42	67·2	3·22	8·49	50·8	42·3
Tool......	·480	1·86	3·41	57·2	2·97	8·16	53·3	45·1
Minor	·500	1·93	3·71	57·4	2·98	10·0	57·8	47·8
“	·550	2·05	3·90	48·2	2·74	11·0	64·1	53·1
Tool......	·560	2·09	3·81	45·4	2·65	10·1	64·5	54·4
Minor	·589	2·12	4·04	41·8	2·55	11·8	68·4	56·6
Drude	·589	2·12	4·04	------	----	------	---	----
Tool......	·600	2·21	4·03	41·3	2·53	11·4	70·4	59·0
Minor	·630	2·22	4·19	37·2	2·41	12·7	73·8	61·1
Drude	·630	2·22	4·19	------	----	------	----	----
Tool......	·640	2·34	4·26	37·8	2·43	12·6	76·6	64·0
Ingersoll .	·65	2·35	4·40	37·6	2·42	13·8	78·3	64·5
Tool......	·680	2·50	4·44	35·3	2·35	13·5	83·1	69·7
Ingersoll..	·87	3·18	5·37	26·0	2·04	18·7	116·	97·6
“ .	1·25	4·50	6·30	14·6	1·55	19·5	183·	164·
“ .	1·75	5·53	6·81	7·03	1·08	15·8	247·	231·
“ .	2·25	5·65	7·18	3·56	0·76	19·5	293·	274·

If we had made use of the average velocity of the electrons instead of assuming the Maxwellian distribution, we should have been led to the expression

$$\sigma=\sigma_0\left[\frac{1+i\dfrac{pm\sigma_0}{Ne^2}}{1+\dfrac{p^2m^2\sigma_0{}^2}{N^2e^4}}\right],$$

the real part of which is the formula given by Schuster and Jeans. It is included here for the sake of a comparison of the results of the two hypotheses as to the electronic velocities.

If now we write S_1 and S_2 for the two series in equation (4)

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* Nicholson, loc. cit.

and substitute the value of σ in equation (1), we obtain on separating the real and imaginary parts

$$n^2\kappa = \frac{8C^2N^2e^4}{p^3m^2\sigma_0}S_1, \quad (5) \quad \text{and } n^2(1-\kappa^2) = K - \frac{4\pi C^2Ne^2}{p^2m}S_2, \qquad (6)$$

in which, in the first terms of each series the value of a is quoted from equation (3). Equation (6) differs from that given by Nicholson (loc. cit.) in that the second term on the right hand side is π times as great.* I am unable, however, to find any error in the formula as given above.

The hypothesis of equal velocities for the electrons yields on similar treatment

$$n^2\kappa = \frac{2\pi C^2N^2e^4}{p^3m^2\sigma_0}\left(1+\frac{\pi}{4a}\right)^{-1} \text{ and } n^2(1-\kappa^2) = K - \frac{4\pi C^2Ne^2}{p^2m}\left(1+\frac{\pi}{4a}\right)^{-1}$$

Thus neglecting the correction terms the values of $n^2\kappa$ are, on this hypothesis, $\pi/4$ times as great as those given by the assumption of the Maxwellian distribution; while to the same approximation the values of $n^2(1-\kappa^2)$ are the same on both hypotheses. Now Nicholson, owing to the absence of the factor π in equation (6), of course finds that the value of $K+n^2(\kappa^2-1)$ on the equal velocity hypothesis is π times as great as on the other. He then uses the values of K yielded by the two formulæ to discriminate between the two hypotheses. This argument, if the formulæ as given above are correct, is illusory. Further, since the value of N is not independently known, it is impossible to discriminate between the two hypotheses by means of the difference between the two results for $n^2\kappa$. The equations resulting from the assumption of the Maxwellian distribution have been adopted for the computations of this paper, because that assumption seems on the whole to the present author to have more inherent probability.

In using equations (3), (5), and (6) for numerical evaluations it is convenient to use, following Schuster, the ratio of the number of free electrons to the number of molecules per unit volume in place of N. Calling this ratio r, we have $N = r/M\tau$, where M is the mass of the hydrogen atom and τ the relative atomic volume. If, to simplify further, we gather together those constants which are the same for all metals, writing $a = e^4/\pi^3m^2M^2C^2$, and use the wave length in vacuo (λ) in place of p, then equations (3), (5) and (6) become

$$\alpha = \frac{\sigma_0{}^2\tau^2}{ar^2\lambda^2}, \quad (7) \quad n^2\kappa = \frac{aCr^2\lambda^3}{\sigma_0\tau^2}S_1, \quad (8) \quad K + n^2(\kappa^2-1) = \frac{C\sqrt{\pi a}\, r\lambda^2}{\tau}S_2, \quad (9)$$

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* In addition there are minor differences in the values of the numerical coefficients in S_1 and S_2.

in which form the equations have been used in this paper for purposes of calculation. It is to be remarked that the series S_1 and S_2 are semiconvergent. That the use of only three terms in either series yields, however, a more than ample accuracy for the purposes in hand, is easily seen. For the ratio of the absolute values of the $(n+1)st$ to the nth terms is in S_1, $(n+1)/a$, and in S_2 $(2n+1)/2a$. Hence S_1 does not begin to diverge until the number of terms is equal to $(a-1)$ and S_2 until the number of terms is $(2a-1)/2$. Thus the best approximation attainable in the use of the series will be, in the case of S_1 when $(a-2)$ terms, and in the case of S_2 when $(2a-3)/2$ terms are employed; the approximation being better the larger the value of a. Now the values of a* for the five metals and the range of the spectrum considered, vary between 12 and 2020. Taking the smallest value of a which occurs, we find by using ten terms that $S_1=0{\cdot}865$ and $S_2=0{\cdot}895$; while by using only three terms, $S_1=0{\cdot}875$ and $S_2=0{\cdot}901$. Thus the error committed in using only three terms is, in this the most unfavorable case, but 1·2 per cent in the case of S_1, and 0·6 per cent in the case of S_2.

We proceed now to the discussion of these equations in the light of the experimental data which we have reviewed. In the first place we observe that equation (8) gives directly the theoretical dispersion of the *product* of the two optical constants. If we assume that r is constant (as seems to be at least tacitly the general impression), the equation expresses a law of great simplicity, namely, that the product of the index of refraction and the coefficient of absorption is proportional to the cube of the wave length of the incident radiation. On account of the variation of a and therefore of S_1 with the wave length, this statement is only an approximate one; but that it very nearly expresses the facts for the five metals under discussion is evident from the circumstance that the maximum variation in S_1 found, is only about 10 per cent. Now that this law is not even remotely fulfilled by the data at hand, will appear on inspection of the fifth column in the tables, where the values of $n^2\kappa/\lambda^3$ as computed from the data of the second, third, and fourth columns are given. Hence we are forced to conclude that r is not a constant, but is a function of the frequency. That is, the number of electrons taking part in the conduction current depends on the frequency of the radiation which sets up that current.

* These are calculated as follows:—a first approximation for r is obtained from equation (8) with $S_1=1$; then with this value of r the first approximation for a is calculated by equation (7); then with this value of a, S_1 and a second approximation for r are computed and thence the second approximation for a. The process is then repeated as often as may be necessary; three approximations being the greatest number required for any of the metals discussed in this paper.

If then, we regard equation (8) as determining r, we have that r varies as $\sqrt{n^2\kappa/\lambda^3}$, the constant of proportionality differing for each substance. The numerical values of r, calculated in this way, are given in the sixth column of the tables and are shown in the figures by the full lines in the upper halves. Owing to the fact already pointed out that the only result of such calculations on which much quantitative dependence can be placed is with respect to *relative* values, the absolute values of r have been computed for only one observer's results in the regions of overlapping; except where there is marked discrepancy in the dispersion.

An inspection of these curves shows in the first place that the numerical values of r are, at the longest observed wave length, of the order of magnitude unity or rapidly approaching such a value. What the value of the ratio would become at infinite wave length cannot be deduced from the equation because S_1 becomes absolutely divergent at very long wave lengths, and because the value of $n^2\kappa$ for zero frequency is unknown. In the second place, it is to be observed that for each metal r increases in value uniformly and in a practically linear manner throughout that portion of the spectrum in which the absorption coefficient has a value in excess of about 4. The point where this approximately linear relation ceases to hold lies in each case either in the red end of the visible spectrum or else not far back in the infra red. And in the third place it is to be noted that the rate of increase of r becomes much greater in the regions of greater transparency (smaller $n\kappa$); and that the value of r does not fall off again after passing through a transmission band, though at the shortest wave lengths observed there is an apparent decrease in its rate of growth.* The magnitude of the ratio at its maximum is, for silver about 16, for copper about 12, for gold 7 to 8, for nickel 2 to 3, and for cobalt 4 to 5.

The fact that this equation of the electron theory leads to the conclusion that the number of free electrons in a metal varies with the frequency of the current does not seem to have been noticed before. The circumstance indicated, that r increases with decreasing absorption becoming in general largest when the absorption is least, does not seem to carry with it any immediately obvious suggestion for an elucidation of the mechanism of the phenomenon. A possible physical explanation may lie in the dual nature generally ascribed to the absorption of light by metals; the first cause being the

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*In the case of cobalt, after an increase of r with decreasing $n\kappa$ similar to that taking place with the other metals, there is a subsequent falling off in r while $n\kappa$ is also rapidly decreasing. Too much emphasis should not be placed on such an anomaly, however, in view of the uncertainties of the data.

taking up of the incident energy by the free electrons, and the second the expenditure of the incident energy in forcing vibrations in the relatively fixed ions. The absorption due to the second cause must be supposed to vary with the wave length in such a way as to be relatively much greater in the neighborhood of those wave lengths corresponding to the natural free periods of the ions. In other words, the ions should produce a "band" type of absorption, the breadth of the bands being proportioned to the range of frequencies to which they are capable of responding. On the other hand, the electrons being free and of small mass should take up energy (if at all) from a much wider range of frequencies, and hence cause a more continuous absorption throughout the spectrum. That the character of the absorption of metals is, for the longer wave lengths at least, of this second type is obvious from an inspection of the curves shown in the several figures. Moreover, as the presence of free electrons is theoretically the distinguishing characteristic of metals in this connection, it is a natural inference that the major part of the absorption of light by metals is due in general to the electrons.

If this is so, then it would be possible to imagine the total absorption due to the two causes to decrease while that due to the second was increasing; and even that there should be a minimum of the total absorption coincident with or nearly coincident with a maximum of the ionic absorption. Then, if in such a resonance region the disturbance within the ions is great enough to set free some electrons, the increase in r would be accounted for. Further, these same considerations would indicate that as the part due to the electrons becomes less, the resultant absorption should change its type, and that it should take on more of the character of the absorption in transparent bodies. That such a change really does occur, the absorption bands at the upper end of the spectrum plainly discernable for silver and indicated for copper and gold would seem to make certain. Further evidence in confirmation of such a change in the type of absorption is offered by the great relative increase in the values of n in the cases of silver, copper, and gold at or after the minimum point of the absorption curve.

The above hypothesis offers no explanation of why the electrons should absorb less of the incident energy at higher frequencies. If it were possible to form a sound dynamical notion as to why the electron with its minute dimensions and mass and simple structure should take up *any* energy from waves which at the shortest used in these measurements are still more than ten million times the electronic diameter, then perhaps the mechanism of the indicated decrease in absorption with increasing frequency would be capable of elucidation.

At present, however, and certainly as far as the experiments under discussion go, there seems to be no light on this question. If the fact of decreasing electronic absorption with increasing frequency be granted, nevertheless, then the above hypothesis appears to be sufficient to reconcile the experimental data.*

It remains to discuss equation (9) in the light of the experiments. Since the values of r can now be regarded as known (from equation (8)), it is obvious that this equation gives us the means of ascertaining the values of K throughout the spectrum. Further it will be seen that the value of K consists of two parts; that due to the term involving r, and that due to $n^2(\kappa^2 - 1)$. The latter is the value of K to be expected if no free electrons were present; hence we may speak of the "dielectric" and the "conductor" parts of K. In order to trace separately the influence of these two parts, the values of each are given in the tables: in column 7 the values of $n^2(\kappa^2 - 1)$ as computed from columns 3 and 4, and in column 8 (headed A) the values of the conductor term as calculated from the right hand side of equation (9). In column 9 is given the algebraic sum of the two terms, or K, which latter is also shown in the broken line curves in the upper halves of the figures.

It is obvious from these results, in the first place, that the values of K are not zero—the value demanded by a perfect conductor. In the second place, we observe that the presence of free electrons (the conductor term) plays the preponderating rôle in the so-called dielectric constant, particularly at the shorter wave lengths. The dielectric term, however, increases relatively to the conductor term with increasing wave length in all of the metals except cobalt. Thus in silver the dielectric term increases tolerably uniformly throughout the region covered by the measurements from about 1 per cent to about 80 per cent of the conductor term; in copper from about 0·1 per cent to 33 per cent; in gold from 1 per cent to 27 per cent; in nickel from 13 per cent to 29 per cent; while in cobalt the proportion varies from 5 per cent through a maximum of

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* It may be possible that the increase in r is to be attributed to a transition layer or region of interpenetration of air and metal. This might naturally be supposed to be relatively poorer in free electrons than the main body of the metal. Then, if at the longer wave lengths the radiation did not penetrate this layer, while at the shorter it did, the increase in r would be explicable. This hypothesis, however, even more than the former, fails to elucidate the mechanism of absorption. If it is adopted it would seem to be necessary to attribute the major part of the absorption to the relatively fixed ions. Hence further assumptions as to the nature and connections of these ions would be necessary, in order to explain the existence of the type of absorption which experiment reveals. However, this is hardly the place in which to follow further such speculations; the experimental basis is not sufficient either in extent or precision.

about 17·5 per cent (at the red end of the visible spectrum) to about 6·5 per cent at the extreme infra-red wave length measured. As in the case of equation (8), it is impossible to predict from equation (9) the relative magnitudes of the two parts for infinite wave length, both because of the divergence of S_2 at large values of λ, and because of lack of knowledge of the value of $n^2(\kappa^2-1)$ under the same circumstances. It is worthy of note also, that the dielectric term is of relatively greater importance at the shorter wave lengths, in the poorer conductors.

Finally we must compare the form of the curves for K as shown in the figures with that demanded by theory. The expressions which have been deduced for K are of the form

$$K = 1 + \sum \frac{k}{\omega^2 - p^2}$$

where k involves the charge, the mass, and the number in unit volume, of the relatively fixed ions; ω is their natural "free" frequency, and the summation is to extend to as many terms as there are such free periods. Now both from the forms of the curves actually found as well as from considerations of inherent probability, it is evident that we have here to deal, not with sharply defined isolated natural periods, but with resonance extending over considerable finite ranges of wave lengths. If we, therefore, transform the formula in the manner of Schuster,* so that it becomes applicable to the cases under consideration, we obtain a quite complicated equation involving the values of the frequencies at the edges of the absorption bands, as well as the constants k.

Now the data at present available for a satisfactory determination of all the constants thus demanded are sufficient neither in extent nor precision, as was remarked earlier in this paper. Nevertheless, it can be stated that the theoretical equation with suitable values of the constants can be made to yield a curve approximating that found, *e. g.*, for silver. It is scarcely worth while to give details of such calculations here, however, as owing to the limitations of the data which have been mentioned, the determination of these constants is largely guess work.

It is to be noted that if we had data available sufficient in extent and precision to permit a satisfactory evaluation of the other constants in such a dispersion formula for K, then that equation would allow us to determine the value of k. This in turn would yield information as to the number of vibrating ions in unit volume just as equation (8) gives us the number

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* Schuster, Theory of Optics, p. 152.

of free electrons. With this added information we should get some light on the magnitude of the part played in the absorption by metals, by the relatively fixed ions; information which could not fail to be of use in unravelling the mechanism of that process.

Summary.

1. From an examination of the available data on the dispersion of silver, copper, gold, nickel, and cobalt, it is concluded that the inaccuracies in the experimentally determined values of the optical constants of these metals are too great to allow of such dependence to be placed on them except for *relative* values. These uncertainties limit seriously the information to be derived from the measurements, and suggests the desirability of obtaining data on the dispersion of mercury, for which metal the causes of the inaccuracies can be eliminated.

2. From a comparison of the data with the dispersion formulæ yielded by the electron theory, it appears

(*a*) That the number of free electrons is not a constant but increases with the frequency of the currents set up by the incident radiation; slowly and uniformly in the infra-red, and more rapidly in the regions where the metals are more transparent. The explanation of this phenomenon is so involved with that of the mechanism of metallic absorption in general, that a wholly satisfactory elucidation of it seems to be impossible at the present time.

(*b*) That the dispersion of the so-called dielectric constant for these metals can be determined. It is seen to consist of two parts, of which that which depends on the presence of free electrons is more important than the other or pure dielectric term, especially at the shorter wave lengths. It also appears that the form of the dispersion curves found is not inconsistent with that demanded by theory, although the inaccuracies of the data do not permit a satisfactory investigation of this point.

Art. XLIII.—*On the Minor Constituents of Meteorites;* by George P. Merrill, Head Curator of Geology, U. S. National Museum.

[Report on an investigation carried on under an allotment from the J. Lawrence Smith fund of the National Academy of Sciences.]

Some three years ago, in view of the current speculations regarding earth history, the writer prepared a paper on "The Composition of Stony Meteorites compared with that of Terrestrial Igneous Rocks."* In the preparation of this paper he was naturally impressed with the comparatively small number of satisfactory chemical analyses that had been made, out of the whole number available but 99 being found which were considered sufficiently complete and accurate for the purpose.† A second impressive fact was the apparent similarity in and simplicity of meteoric composition, there being shown scarcely any of those elements which recent rock analyses have found to be common constituents, though in very small quantities, of terrestrial rocks. These facts, coupled with the occasional reported occurrences of such elements as platinum, gold, tin, lead, zinc, etc., and the high degree of perfection reached by modern analytical chemistry, suggested the advisability of undertaking a systematic investigation of the chemical nature of both stone and iron meteorites, with particular reference to the occurrence of such elements as had been reported as doubtful or found only in traces. On mentioning the matter to Prof. Morley, I was encouraged to make application for financial assistance from the J. Lawrence Smith fund of the National Academy of Sciences. This was promptly granted; without it the work, under conditions now existing, would have been impossible. There being no analytical chemist attached to the Museum staff, and as naturally none of those employed in other branches of the Government service could be spared, it became necessary to employ someone in commercial life. Looking over the available field, I was fortunately reminded of Dr. J. E. Whitfield, now with Booth, Garrett & Blair, of Philadelphia, but at one time with the U. S. Geological Survey, who while there employed had made himself fully conversant with the difficult and complicated methods of analyses essential to a satisfactory understanding of these bodies.

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* This Journal, xxvii, 469–74, 1909.

† Farrington made use of 125 in his more recent study (Analyses of Stone Meteorites, Pub. 151, Geol. Series, vol. iii, No. 9, Field Museum of Natural History).

As is well known, the non-gaseous elements characteristic of meteorites the presence of which have been established by quantitative methods beyond controversy are silicon, aluminium, iron, chromium, manganese, nickel, cobalt, magnesium, calcium, sodium, potassium, sulphur, phosphorus and carbon. In addition there have been reported, usually under such conditions as to need authentication, or at least corroborative testimony, arsenic, antimony, copper, gold, lead, palladium, platinum, tin, titanium, tungsten, uranium, vanadium and zinc. It was mainly for the purpose of fixing the presence or absence of these last named in amounts sufficient for determination by a skillful analyst that the investigation was undertaken, though the possible occurrence of other elemental constituents of terrestrial igneous rocks was not ignored. When possible, samples of the same meteorities in which a doubtful element had been reported were utilized. In others, meteorites were taken which had not before been subject to analysis. The investigations were performed upon amounts of not less than 50 grams each, and each sample was carefully selected in order to insure its correctly representing the entire mass. In all cases the meteorite has been made the subject of careful study—if a stone, in thin sections—in addition to the analysis.

Before discussing my own results, it may, however, be well to enter into some detail regarding the previously reported occurrences of the unusual constituents.

Arsenic.—The first determination of arsenic of which I have record is that of Karl Rumler, who in 1840 reported* getting distinct arsenical reactions from the olivine-like mineral occurring in both the Atacama, Bolivia, and the Krasnojarsk, Siberia, pallasites. It is difficult to detect possible sources of error in Rumler's method as given. The fact, however, that no one has since been able to corroborate his work would suggest some possible impurity in his reagents. The only other reported occurrence of arsenic known to me is that of Fischer and Duflos in the Braunau iron.† The determination can to-day scarcely be considered satisfactory. The solution remaining after the precipitation of the copper was evaporated, the dry residue mixed with soda and heated before the blowpipe; result, a garlic odor. In stating the analysis, copper, manganese, arsenic, lime, magnesium, silicon, carbon, chromium, and sulphur are all thrown together as amounting to 2·072 per cent.

Antimony.—Traces of this metal were reported by Trottorelli in the stone of Collescipioli. I have not seen the original paper, but an abstract by Max Bauer‡ gives, among other con-

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* Pogg. Ann., xlix, 591, 1840.

† Pogg. Ann., lxxii, 479, 1847.

‡ Neues Jahrb. für Min., etc., 1891, ii, 238.

stituents, lead, antimony, tin and lithia as occurring in traces, palladium to the amount of 0·7745 per cent, and soda (Na_2O) to the unheard of amount of 10·386 per cent! I have, therefore, a natural feeling of scepticism regarding the results as a whole.

Copper.—Copper in amounts from traces up to weighable quantities has been reported by such authorities as Rammelsberg, Rose and J. L. Smith, and should be removed from the doubtful list.

Gold.—Gold, so far as I am aware, has been suggested as a constituent of but a single meteorite, that by A. Liversidge* in an iron from Boogaldi, New South Wales. Notwithstanding the fact that the work of Prof. Liversidge seems to have been performed with proper care, there exists a lingering doubt in the minds of many as to the actual occurrence of this element as an original constituent of the iron.

Lead.—Trottorelli, whose analysis is above referred to, reported traces of lead in the Collescipioli stone. R. P. Greg also reported† native lead lining the cavities in an iron from the Tarapaca desert of Chile. J. L. Smith, however, concluded from his own examination‡ that the metal was altogether foreign to the stone when it fell.

Lithia.—Lithia was reported by Story Maskelyne§ to the amount of 0·016 per cent in the enstatite and in traces in the augitic constituent of the Busti stone. J. L. Smith likewise reported‖ traces of lithia in the stones of Waconda, Kansas, and Bishopville, South Carolina. Others report it determined by spectroscopic methods.

Platinum, palladium, and iridium.—Platinum, palladium, and iridium come in for occasional reference as meteoric constituents, but almost invariably in amounts too small to weigh, and often in analyses made under such conditions as to give rise to a feeling of doubt as to their correctness. Trottorelli's reported finding of platinum has already received attention. J. M. Davison¶ obtained from 608·6 grams of the Coahuila iron 0·014 grams of platinum; from 464 grams of the Toluca iron a few crystals of potassium platinic chloride were obtained which showed a reddish color and probably contained iridium. Tassin** reported the soluble portion of the Persimmon Creek iron as containing traces of platinum too small to weigh. Mallet's work on the Canyon Diablo iron is likewise confirmatory. (See page 514.)

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* Journ. and Proc. Roy. Soc. of N. S. W., vol. xxxv.

† Phil. Mag., x, 12, 1855; also this Journal, xxiii, 118, 1857.

‡ This Journal, xlix. 305, 1870.

§ Philos. Trans. Roy. Soc., clx, 206–7, 1870.

‖ This Journal, xiii, 212, 1877; xxxviii, 226, 1869.

¶ Ibid., vol. vii, 1899.

** Proc. U. S. Nat. Mus., xxvii, 959, 1904.

Tin.—Tin to the amount of 0·17 per cent SnO_2 was reported[*] by Stromeyer and Walmstedt as long ago as 1825 as occurring in the olivine of a pallasite. Unfortunately some doubt exists as to whether this was the pallasite of Krasnojarsk or Steinbach. Rammelsberg in 1884[†] reported finding 0·08 per cent Sn in the metallic portion of the Klein-Wenden aërolite, and he also tabulates[‡] 0·57 per cent Sn in the analysis of the Nashville (?), Tennessee, iron. Jackson[§] thought to have found 0·063 per cent Sn in an iron from Dakota, while C. A. Joy reported[‖] 0·44 per cent SnO_2 in the mineral portion of the Atacama pallasite, and Mallet reported[§] ·002 to ·003 per cent Sn in the iron from Staunton, Virginia. Numerous other occurrences of like small amounts are mentioned in the literature, the copper and tin being frequently undifferentiated. Although not so stated, the inference may be drawn, with the possible exception of that found in the olivine above noted, that tin, if present at all, occurs mainly, if not wholly, as a constituent of the metallic portion of the meteorite.

The occurrence of this metal has for a long time been regarded as open to question by the writer, notwithstanding the apparent care and skill under which the various analyses had been made. The scepticism was based in part upon the conditions under which the metal occurs in terrestrial rocks, where, as is well known, its presence is limited almost wholly to acidic rocks of the granitic type; in but two exceptions has it been found to occur in rocks of intermediate (andesitic) type. Genetically then it is fair to assume there is some connection. Among the common mineral associations of terrestrial tin, in the form in which it usually occurs—cassiterite—are, further, several characteristic species, such as fluorite, tourmaline, wolframite, topaz, etc., which are utterly unknown in meteorites. It is of course possible that tin, if present, is in the form of the sulphide—stannite—or as an alloy with iron, but none of the recorded analyses of meteoric sulphides show a trace of the element, nor do analyses of terrestrial irons, as those of Ovifak, Greenland, or the various terrestrial nickel irons as josephinite, awaruite, etc.[**]

Titanium.—Rammelsberg[††] found 0·16 per cent titanic oxide (TiO_2) in the insoluble residue from the Juvinas stone. This is the first reported occurrence. Davison reported[‡‡] traces of

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[*] See Rose, Beschreibung u. Eintheilung der Meteoriten, etc., 1864, p. 77.

[†] Pogg. Ann., lxii, 449.

[‡] Die Chemischer Natur der Meteoriten, 1870, p. 146.

[§] This Journal, xxxvi, 260, 1863.

[‖] Ibid., xxxvii, 245, 1864.

[¶] Ibid., ii, 1884.

[**] These analyses are brought together in convenient form and discussed on pp. 313–15, 2d ed. of Clarke's Data of Geochemistry.

[††] Pogg. Ann., lxxiii, 585, 1848.

[‡‡] This Journal, xxii, 59, 1906.

titanium in the stone from Estracado, Texas. Everhart[*] found 0·09 per cent in that of Pickens County, Georgia; and Stokes[†] found 0·08 per cent in the stone of Allegan, Michigan. These occurrences are all dwarfed by Tschermak's[‡] determination of 2·39 per cent in the stone of Angra dos Reis. The amounts are, however, mostly very small and, knowing the difficulties in the way of determination, it seems probable that it is a more common and widespread constituent than is commonly supposed.

Vanadium.—Apjohn reported[§] finding unmistakable evidences of vanadium in the Limerick stone, but in amount too small for quantitative determination.

Zinc.—E. Pfeiffer, in the report[‖] of his analysis of the Parnallee stone, included traces of copper, tin, and zinc. J. L. Smith[¶] found in the schreibersite from the Tazewell iron a trace of zinc. I find no other recorded occurrence of this element.

But eleven meteorites have thus far been subjected by us to the exhaustive treatment necessary to confirm or refute these reported occurrences. Five are stones, two stony irons, and four are irons. The results are given below.

(1) Iron. Canyon Diablo, Arizona. A coarse octahedrite iron with numerous interlaminations of schreibersite and inclusions of graphite and troilite, the latter sometimes an inch or more in diameter. In the selection of samples for analyses these were avoided as far as possible. Carbon is present in form of microscopic diamonds and also as graphite. It has been the subject of numerous analyses, yielding variable results owing to its coarse crystallization. Whitfield's analysis is given in column I below. In column II is given the average of three analyses by Moissan, Booth Garrett and Blair, and Tassin.

	I	II
Silicon	trace	0·032%
Sulphur	0·009%	0·007
Phosphorus	0·261	0·159
Manganese	none	none
Copper	0·015	trace
Nickel	7·335	5·828
Cobalt	0·510	0·044
Combined carbon	0·105	0·465
Graphitic carbon	0·028	

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[*] Science, xxx, 772, 1909.

[†] Proc. Wash. Acad. Sci., ii, 48, July, 1900.

[‡] Tsch. Min. petr. Mitt., xxxviii, 110, 1909.

[§] Journ. Chem. Soc., London, xxvii, 104, 1874.

[‖] Sitz. k. k. Acad. der Wiss. Wien, xlvii, 461, 1863.

[¶] This Journal, xix, 155, 1855.

	I	II
Iron oxides	2·520%	----
Iron protochloride	0·097	----
Iron	89·167	93·425%
	100·047	99·96

In process of analysis schreibersite to the amount of 1·832 per cent was separated out. This has the following composition:

Iron	55·04%
Nickel	29·58
Phosphorus	15·38

Platinum was looked for in two portions of fifty grams each, but none was found. Neither is its presence recorded in previous analyses by this same firm, by Derby,[*] Tassin or Moissan.[†] J. W. Mallet, working on a residue from the solution of 25 pounds of the iron in dilute hydrochloric acid, obtained results representing 3·63 grams of platinum and 14·95 grams of iridium per metric ton of the original iron, "with probably a trace of rhodium." He suggests that the platinoid metals are not uniformly distributed in the iron.[‡] This may account for the failure to find it on the part of others. The quantity of material worked upon is undoubtedly an important factor, however.

(2) Iron. Casas Grandes, Mexico. Medium octahedrite. Previously analyzed and described by Tassin.[§] The results of Dr. Whitfield's analysis are given in column I below. In column II are given Tassin's results as previously obtained.

	1	II
Silicon	0·010%	----
Iron	90·470	95·13%
Nickel	7·742	4·38
Cobalt	0·604	0·27
Copper	0·012	trace
Phosphorus	0·166	0·24
Sulphur	0·029	none
Combined carbon	0·145	traces
Graphitic carbon	0·032	
Iron oxides	0·794	----
	100·004	100·02

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[*] This Journal, xlix, 101–110, 1895.

[†] See Contributions to the Study of the Canyon Diablo Meteorite, by G. P. Merrill and W. Tassin, Smith. Misc. Colls., Quar. Issue, 1, pt. 2, p. 209.

[‡] Proc. Acad. Nat. Sci. Phila., Dec., 1905, 913; footnote on p. 862.

[§] Proc. U. S. Nat. Mus., xxv, 69–74, 1902.

Dr. Whitfield's analyses were made on 50-gram samples, free from evident inclusions of troilite. The following elements were looked for but not found; antimony, tin, lead, palladium, platinum, titanium, tungsten, vanadium, uranium, chromium, manganese, molybdenum and zinc.

(3) Iron. Mount Joy, Pennsylvania. Coarse octahedrite; brecciated. Previous analysis by Eakins* yielded:

Iron	93·80%
Nickel	4·81
Cobalt	0·51
Copper	0·005
Phosphorus	0·19
Sulphur	0·01
	99·325

Further tests by Dr. Whitfield on a 50-gram sample yielded:

Chromium	0·006%
Manganese	0·075
Copper	0·008
Chlorine	0·255
Platinum	trace

No vanadium, molybdenum, tungsten, gold, silver, lead or tin, nor in fact any other element in amounts large enough to be determined by wet analysis, were found.

(4) Iron. Perryville, Missouri. Described by Merrill† as belonging to Brezina's group of finest octahedrites (Off.). As the entire iron was in possession of the National Museum and it had not before been described, all the necessary material was sacrificed for a very detailed analysis, with the results tabulated below:

Iron (by difference)	89·015%
Nickel	9·660
Cobalt	0·545
Copper	0·025
Manganese	none
Phosphorus	0·365
Sulphur	0·002
Silicon	0·003
Carbon	0·015
Iridium Palladium Platinum Ruthenium	traces
	99·63

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* This Journal, xliv, 416, 1892.

† Proc. U. S. Nat. Mus., xliii, pp. 595–97, No. 1943, 1912.

The amount of the rarer elements found in different samples of this iron was quite variable, but always small. From one portion of 25 grams was obtained 0·004 gram of platinum and from another portion of 100 grams weight but 0·0002 gram. The precipitates of ammonium platinic chloride were in all cases faintly orange, indicating the presence of palladium but in amounts too small for determination. In a 100-gram sample of the iron were found 0·014 gram of ruthenium and 0·028 gram of iridium, while another portion of equal weight yielded but 0·0009 gram of ruthenium and 0·0011 gram of iridium. So far as I am aware, this is the first recorded occurrence of ruthenium in a meteoric iron. The probable presence of iridium in the Toluca and Coahuila irons was recognized by Davison, as already noted, but is not elsewhere recorded.

No chromium, vanadium, molybdenum or titanium were found. The mineral schreibersite, constituting 2·61 per cent of the iron, was isolated and analyzed with the following results:

Phosphorus	14·00%
Iron	51·10
Nickel	34·13
Cobalt	0·30
	99·53

This high percentage of nickel is comparable with that of the schreibersite from the Magura iron. Even greater amounts have been reported as yielded by the irons of Seelasgen, Germany (36·17 per cent), and Cranbourne, Australia (38·24 per cent).

(5) Stony iron (Pallasite). Mt. Vernon, Kentucky. A coarse pallasite, consisting of large blebs of olivine in a mesh of metal. Described by Tassin.* No complete (bulk) analyses made owing to the coarse nature of the stone. The nickel-iron alloy yielded Tassin as follows:

Iron	82·520%
Nickel	14·044
Cobalt	0·949
Copper	0·104
Sulphur	0·288
Silica	0·808
Aluminum	0·410
Carbon	0·465
Phosphorus	0·390
Chlorine	trace
	99·978

He also gave analyses of the included tænite, schreibersite, troilite, chromite and olivine separately, but found no constituents of unusual occurrence.

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* Proc. U. S. Nat. Mus., xxviii, 213, 1905.

A 50-gram sample, badly oxidized, submitted to Dr. Whitfield for tests for minor elements, yielded:

Chromium	0·300%
Copper	0·016
Nickel	2·960
Cobalt	0·090
Manganese	0·151
Vanadium	trace

No trace of molybdenum, tungsten, antimony, tin, lead, zinc, gold, silver, or platinum was found.

(6) Meteoric stone. Selma, Alabama. Described by Merrill,* but no analysis given. Examination of thin sections showed the presence of the usual metallic particles together with olivine, enstatite and a monoclinic pyroxene.

A bulk analysis by Whitfield yielded results as follows, all the iron being considered for the time being as ferric:

Silica (SiO_2)	32·40%
Alumina (Al_2O_3)	4·88
Iron oxide (Fe_2O_3)	37·00
Chromic oxide (Cr_2O_3)	0·19
Lime (CaO)	1·52
Magnesia (MgO)	21·05
Manganous oxide (MnO)	0·27
Nickel oxide (NiO)	1·88
Cobalt oxide (CoO)	0·12
Vanadic oxide (V_2O_3)	trace
	99·31

Considering the metallic portion alone, the results were as follows:

Total iron	25·866%
" chromium	0·127
" nickel	1·470
" cobalt	0·090
" manganese	0·210
" vanadium	trace

All the other constituents noted above under 5 were absent.

(7) Meteoric stone. Ness County, Kansas. Described by H. L. Ward.† No analysis given. The stone was somewhat decomposed through weathering, but yielded approximately 15 per cent of nickeliferous iron, which showed:

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* Proc. U. S. Nat. Mus., xxxii, 59.

† This Journal, vii, 233, 1899.

Copper	0·30%
Nickel	7·00
Cobalt	0·20
Iron	92·04
	99·54%

A bulk analysis, in which all the combined and oxidized iron was determined as ferric oxide, yielded:

Silica (SiO_2)	38·340%
Ferric oxide (Fe_2O_3)	8·551
Alumina (Al_2O_3)	8·259
Chromic oxide (Cr_2O_3)	0·587
Lime (CaO)	1·180
Magnesia (MgO)	24·040
Metal (FeNi)	15·000
Loss on ignition	3·500
	99·457

Recalculating the first analysis in order to include the components of the metallic portions, and thus obtain the composition of the stone as a whole, we have:

Silica (SiO_2)	38·340%
Ferric oxide (Fe_2O_3)	8·551
Alumina (Al_2O_3)	8·259
Chromic oxide (Cr_2O_3)	0·587
Lime (CaO)	1·180
Magnesia (MgO)	24·040
Loss on ignition	3·500
Iron (Fe)	13·860
Nickel (Ni)	1·050
Cobalt (Co)	0·030
Copper (Cu)	0·050
	99·447%

None of the rarer elements were found.

(8) Meteoric stone. Cullison, Kansas. Described by Merrill.* Thin sections showed it to be of the normal chondritic type containing olivine, enstatite, monoclinic pyroxene, plagioclase feldspar, with the usual sprinkling of metal and metallic sulphides. The separation of the component parts by an electro-magnet and treatment with iodine resulted as follows:

Troilite	6·07%
Metal	19·40
Silicates	74·50
Schreibersite	0·10
	100·07%

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* Proc. U. S. Nat. Mus., xliv, pp. 325–30, 1913.

The metallic portion yielded :

Silicon	0·129%
Sulphur	trace
Phosphorus	0·071
Nickel	9·207
Cobalt	0·507
Copper	0·040
Chromium	0·160
Carbon	0·088
Manganese	0·080
Iron	89·700
	99·982

with no traces of tungsten, vanadium or molybdenum. The silicate portion yielded :

Silica (SiO_2)	47·36%
Alumina (Al_2O_3)	5·67
Ferric oxide (Fe_2O_3)	0·10
Ferrous oxide (FeO)	11·25
Iron (Fe)	0·84
Magnesia (MgO)	31·72
Manganous oxide (MnO)	0·36
Soda (Na_2O)	2·42
Potash (K_2O)	0·23
Titanium (Ti)	none
	99·95%

Combining the metallic and non-metallic portions and recalculating with the usual assumption that the mineral called troilite is the monosulphide FeS, and that the schreibersite conforms to the formula Fe_2NiP, the following figures are obtained representative of the composition of the stone as a whole :

Silica (SiO_2)	35·300%
Alumina (Al_2O_3)	4·24
Ferric oxide (Fe_2O_3)	0·75
Ferrous oxide (FeO)	8·38
Lime (CaO)	0·62
Magnesia (MgO)	23·631
Manganous oxide (MnO)	0·268
Soda (Na_2O)	1·804
Potash (K_2O)	0·171
Sulphur (S)	2·184
Phosphorus (P)	0·0138
Nickel (Ni)	1·80

Cobalt (Co)	0·098%
Copper (Cu)	0·008
Chromium (Cr)	0·029
Carbon (C)	0·017
Manganese (Mn)	0·015
Iron (Fe)	21·270
	100·5988

None of the rarer elements, other than those noted, were found.

(9) Meteoric stone. MacKinney, Collin County, Texas. Referred to by Brezina* and relegated to his Cs type, characterized by colorless chondrules firmly imbedded in a dark gray to black ground. The mineral composition and structure are given but no analyses. Dr. Whitfield found the stone to consist of:

Troilite (FeS)	6·26
Schreibersite	0·58
Metal	5·70
Chromite	0·11
Silicate minerals	87·35
	100·00

The silicate portion yielded:

Silica (SiO_2)	43·30%
Alumina (Al_2O_3)	15·18
Ferrous oxide (FeO)	8·45
Lime (CaO)	1·88
Magnesia (MgO)	30·48
Manganous oxide (MnO)	0·25
Nickel oxide (NiO)	0·51
	100·05%

The metallic portion yielded:

Iron (by difference)	85·84%
Cobalt	0·92
Copper	0·08
Nickel	13·16
	100·00%

Barium, strontium and zirconium, in addition to the other rarer elements, were looked for but no traces discovered.

(10) Meteoric stone. Holbrook, Arizona. Described by Merrill.† A gray chondritic stone, very fresh, having fallen

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* Ann. K. K. Hofmus., x, p. 252, 1895 (96).

† Smithsonian Miscellaneous Collection, lx, No. 9, pp. 1–4, 1912.

on July 19th of the present year. Contains very little metallic iron, but is correspondingly rich in sulphide. Analyses by Whitfield yielded:

Schreibersite	0·11%
Troilite	7·56
Metal	4·85
Silicates	87·48
	100·00%

The metallic portion yielded:

Nickel	8·68%
Cobalt	0·64
Copper	0·29
Iron	90·50
	100·11%

The silicate portion yielded:

Silica (SiO_2)	41·93%
Alumina (Al_2O_3)	4·30
Ferrous oxide (FeO)	21·85
Lime (CaO)	2·40
Soda (Na_2O)	trace
Magnesia (MgO)	29·11
Manganous oxide (MnO)	0·25
Nickel oxide (NiO)	0·08
	99·92%

None of the rarer elements under consideration were found, even in traces. The sulphide occurs in such forms as to be readily separated mechanically, and yielded on analysis:

Iron	63·62%
Sulphur	36·50
Nickel, cobalt and copper	none
	100·12%

This analysis shows the mineral to be troilite, though its specific gravity (4·61) is low. It is, however, wholly unattracted by the magnet and apparently there is no question as to its true nature. Its occurrence in this form is interesting in a stone so low in the metallic constituent.

(11) In addition to the above recorded analyses a 26-gram fragment of the Krasnojarsk pallasite was sacrificed in a search for arsenic and tin. No trace of either was found.

The results recorded in the preceding pages afford opportunity for interesting comparisons between the meteorites and terrestial rocks, matters to which attention was called in the paper above referred to, but which with the additional data now at hand can be elaborated. The meteorites, as there shown, are in any degree comparable only with the most basic of terrestrial igneous rocks, mainly with the peridotites or pyroxenites, rarely with the basalts. Omitting the silicates common to both groups and limiting consideration to the metallic and minor constituents, we find, first, nickeliferous iron and iron phosphides almost universally present in meteorits, but rare in terrestrial rocks. Exceptions must be made in favor of the iron in the Greenland basalt, and the more recent discovery of native iron in the basalt of Buhl, Germany,* besides a few minor occurrences in basalts and diabases. Sufficient for now that it does occur, though rarely, as is to be expected from the energetic oxidizing disposition of our atmosphere. Iron sulphides are common to both groups, though it is apparent that the idea first promulgated by Rose to the effect that the monosulphide troilite is limited to certain classes of meteorites is erroneous.

Carbon, either as diamond, graphite, or an amorphous condition, or again as CO, CO_2 or as a hydrocarbon of uncertain formula, is now recognized as a common constituent of meteorites,† both stony and iron. Except as in form of the diamond, however, this element has, so far as I am aware, never been reported in terrestrial peridotites, though it does occur in the metalliferous portions of the iron-bearing basalt of Greenland. Where occurring in igneous rocks it is with this exception wholly in those of a granitic or syenitic type.

In Washington's compilation of analyses‡ there are reported among the unusual elements of terrestrial peridotites, only; (1) titanium, (2) phosphorus, (3) manganese, (4) zirconium, (5) strontium, (6) boron, (7) nickel, and (8) vanadium. Whether or not other elements were looked for is not stated, but from what is known of the character of the analysts it is safe to assume that they were. Eakins, in a wehrlite from Red Bluff, Montana, reported§ 0·81 per cent TiO_2; 0·12 per cent P_2O_5; 0·08 per cent MnO; 0·16 per cent NiO; and a trace of BaO. Also in a peridotite from Silver Cliff, Colorado, 0·17 per cent P_2O_5 and 0·40 MnO. Hillebrand, in an analysis of a peridotite from Opin Lake, Marquette region, Michigan, found 0·66 per cent TiO_2; 0·17 per cent P_2O_5; 0·12 per cent MnO; with traces of BaO and SrO. The same authority found 0·26 per cent TiO_2 with traces of P_2O_5 and ZrO_2; 0·22 per cent MnO;

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* F. F. Hornstein, Centralblatt Min., 1907, p. 276.

† See Cohen's Summary, Meteoritenkunde, vol. i, pp. 138–82.

‡ Professional Paper, No. 14, U. S. Geological Survey.

§ Prof. Paper, No. 14, U. S. Geological Survey.

0·03 per cent NiO, and 0·03 per cent V_2O_3, with no BaO or SrO in a websterite from Cecil County, Maryland. A dunite from the Tulameen River in British Columbia yielded the same authority no TiO_2, BaO, ZrO_2 or SrO; only traces of P_5O_5, but 0·10 per cent of NiO. Neither copper nor tin is reported in any instance. On the other hand there are found in the meteoric peridotites both copper and tin (?), together with platinum and vanadium. The last named, as is well known, has been shown to be a widely distributed element, though occurring in minute quantities and in the less siliceous rocks.* In rocks rich in olivine and ferrous iron (i. e. peridotite) it is, however, so far as available analyses show, wholly lacking. Although platinum is known to occur even in commercial quantities in some peridotites, Duparc's analyses† failed to reveal it: this is unquestionably owing to the small amount of rock operated upon. The lack of more definite results on meteoric peridotites may doubtless be ascribed to the same reason.

Silica or silicon is not infrequently reported in analyses of meteoric iron in amounts rarely exceeding 0·2 of one per cent. The condition under which the element exists is in some cases at least problematical. Hunt and Silliman, in describing the iron of Lockport (Cambria), N. Y.,‡ refer to a reddish brown residue obtained by them as being "either silica with a trace of carbon or silicon," which last, they add, "Prof. Shepard has already shown to exist in the Oswego iron." Prof. Shepard, however, in his paper simply tabulates his results as "Silicon 0·20 per cent" and does not commit himself as to the condition under which the element may exist. Prof. Mallet, in his analysis of the Staunton, Va., iron, gives 0·067 per cent, 0·061 and 0·056 per cent SiO_2, but adds by way of explanation, "some of it (i. e., the Si) seems to have in reality existed as a silicate of iron."§ Cohen, in his Meteoritenkunde (p. 55), refers the Ca, Mg, Al, K and N very properly to the silicate minerals, and adds, "Das gleiche gilt wohl auch in der Regel für Silicium; doch führte Winkler in metallischen Theil von Rittersgrün gefundene Kieselsaure auf Silicium zurück, welches mit Eisen verbunden war, und nahm das Vorhandensein eines Siliciumeisen von der Formel Fe_2Si an, dessen Menge er für das Nickeleisen zu 0·329 per cent berechnete." W. Tassin in 1907 announced verbally in an informal communication before the National Academy of Sciences "the discovery of elemental silicon" in the meteoric iron of Casas Grandes, Mexico, incidentally claiming it as "the first announcement of the occurrence of this element in nature." With reference to these

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* Bull. 167, U. S. Geol. Surv., 1900, p. 49. Also Clarke, The Data of Geochemistry, p. 672.

† Arch. Sci. Phys. Nat., xxxi, 194.

‡ This Journal, ii, 374, 1846.

§ Ibid., ii, 1871.

reports it may be stated that an examination of the insoluble residues from all of these irons reveals the presence of minute particles of quartz, sometimes shreds of glass and sundry silicates.* It would seem most probable, therefore, that the small percentage of the element found had existed either as free quartz (SiO_2) or as a silicide of iron. Until the element shall be actually isolated it is certainly unsafe, if not absurd, to claim its existence in other form than that of a condition of combination with other elements.

In résumé, then, the elements heretofore reported, but the presence of which this investigation not merely fails to confirm but throws grave doubts on previous determinations, are antimony, arsenic, gold, lead, tin, tungsten, uranium, and zinc. The occasional presence of platinum is apparently confirmed beyond question, and, in two instances, of vanadium; palladium and ruthenium have also been found in a single instance. The presence of platinum was to be expected from the analogy with the terrestrial sources of this metal. Vanadium and titanium were also not unexpected in view of their widespread occurrence in terrestrial rocks as shown by Hillebrand's analyses already referred to. The absence in meteorites of certain other constituents, such as strontium, barium, and zirconium, cannot yet be so readily explained. A much larger series of analyses is necessary, and it is suggested further that future analysts state not merely what is found, but what is looked for *and not found.*

Supplemental note.—Farrington's statement† with reference to the conclusions given in my paper referred to on p. 509, that in comparisons of this nature only the more silicious meteorites should be used, is unjust to me since I made comparisons not merely of the composition of meteorites as they are, but of the same with all the iron eliminated (see p. 473 of my paper), considering thus the most acid phase conceivable, not even omitting the wholly anomalous Bishopville stone. Further, I do not regard as sound the statement "That the earth's crust

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* See Cohen and Weinschenk on the Toluca, Mexico, meteoric iron, Meteoreisen Studien, Ann. K. K. Hof. Mus., 1891, p. 140. It should be added, however, that personally I regard the pre-terrestrial origin of these particles as open to serious doubt. In residues from a quantity of shavings from the Casas Grandes iron and from a 10-gram piece showing a portion of the original surface, though carefully cleansed, I found easily recognizable, clear, glassy quartz, both in form of crystals and glassy fragments, shreds of colorless glass and also undeterminate silicate minerals. Two other determinations on pieces cut from a depth of two centimeters below the surface yielded no such results, the residues being clean graphitic particles and schreibersite flakes. A few minute, colorless isotropic particles, too small to manipulate, were crushed under the microscope between glass slides and were found to scratch and bite into the glass with all the energy of the diamond.

† Publ. 151, Field Mus. Nat. Hist., Geol. Series, vol. iii, No. 9, 1911.

of earlier times was more nearly meteoric in composition than the present seems to be indicated by the great deposits of iron oxide of earlier ages and the fact that the early limestones are more magnesian than the modern." That the older rocks contain a larger proportion of these substances than the more recent is unquestionable, but such are products of secondary accumulation and cannot be accepted as proof of early abundance. The greatest deposits of iron ore of which we have knowledge are merely secondary or results of leaching of lean ores in the older rocks and a concentration of much more recent date. Whether we accept the early views to the effect that the Lake Superior ores were due wholly to leaching from lean, cherty carbonates or greenalite beds and reconcentration, or the more recent ideas of Van Hise and others,* that the main mass of the iron-bearing sediments was derived from associated eruptive rocks, we have to look for the original source of the material to rocks not richer in iron than those of very recent origin. Concentration has simply gone on for a longer period and the results are naturally of greater magnitude. This is recognized by Van Hise.† In discussing the origin of the ores of the Menominee district he says, "the process of ore concentration was well advanced before Cambrian time." In the Mesabi district "the concentration was well advanced as early as Cretaceous . . . and the process of enrichment has undoubtedly continued until the present time. It therefore appears that the circulating waters have had eras in which to perform their work; indeed a part of the pre-Paleozoic time and all of the Paleozoic, Mesozoic, and Cenozoic." A like analysis will dispose of the argument relative to the presence of magnesia in the older rocks. Dolomitic rocks are now, I believe, universally recognized in the majority of cases as due not to original sedimentation, but to a gradual replacement of lime by magnesia through the downward percolation of very dilute magnesian waters.‡ There is no reliable evidence showing that early sea waters were richer in magnesian salts than those of to-day; that more magnesia is to be found in the older limestones is due wholly to prolonged periods of a process of concentration still in operation.

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* Monograph 52. U. S. G. S., The Geology of the Lake Superior Region.

† Loc. cit., p. 558.

‡ See Rep. of Coral Reef Com. Royal Soc. of London, 1903; also Clarke's Summary, Bull. 491, U. S. G. S., pp. 534–45.

Art. XLIV.—*Results of a Paleobotanical Study of the Coal-bearing Rocks of the Raton Mesa Region of Colorado and New Mexico*:* by F. H. Knowlton.

The Raton Mesa region comprises an area about 90 miles long by 50 miles wide, lying along the east front of the Rocky Mountains and extending from near Walsenburg, Colorado, on the north, to the Cimarron River, New Mexico, on the south. The coal beds within this area are numerous and extensive and have long been mined and exploited. The object of the present paper is to show the pronouncement of the fossil flora on the question of the age of the coal-bearing formations involved.

Although the presence of coal in this region had long been known, the first to bring back any paleobotanical evidence bearing on its stratigraphic position apparently was Lt. T. W. Abert, who visited New Mexico under conditions of the greatest hardship in the winter of 1846. The coal was presumed to be similar to that of the Missouri region—namely, Carboniferous—but the finding of modern-appearing dicotyledonous leaves both above and below it showed of course that it was very much younger, though no attempt was then made to fix its position more exactly.

The first plants from the region to pass under scientific eyes were obtained in July, 1867, by Dr. John L. LeConte while serving as geologist on one of the Pacific Railroad surveys. These plants came from beds now know to be in the upper part of the section. They were studied by Lesquereux, who pronounced them to be of Tertiary age. LeConte, however, considered the beds as Cretaceous in age from the presence of certain marine invertebrates, though these were not found in place.

In 1869 a considerable collection of plants was secured from the Fisher's Peak region by Dr. F. V. Hayden, and his account of their occurrence, together with a description of the general geology of the region, is presented in his Third Annual Report. These plants also were studied by Lesquereux, who referred them to the Eocene and at the same time pointed out their undoubted affinity with Lower Tertiary (Eolignitic) flora of Mississippi.† In 1872 Lesquereux himself visited the region and added a few species, among them being apparently the first to be obtained from the lower coal-bearing rocks, now known as the Trinidad sandstone. In 1878 Lesquereux published his *Tertiary Flora*,‡ in which he brought together all the scat-

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* Published with the permission of the Director of the U. S. Geological Survey.

† 5th Ann. Rept. U. S. Geol. & Geogr. Serv. Terr., 1872, Suppl., p. 19.

‡ Rept. U. S. Geol. Surv. Terr., vol. v, pp. 1–366, pls. i–lxv, 1878.

tered Tertiary material from the Rocky Mountain region, and for the first time adequately described and figured it; there was no change in his opinion regarding the stratigraphic position of the Raton Mesa material.

From 1878 to about 1905, which later date marks the renewal of interest in this field, work on the paleobotany of the Raton Mesa region was desultory and relatively unimportant. About 1883 Doctor Newberry obtained and described a few species, also from the upper beds. About the time Newberry wrote, the age of the beds had come to be regarded as Laramie, apparently on the mistaken assumption that they were of the same age as the coal-bearing rocks of the Denver Basin which had then come definitely to be known as Laramie. From that time until the work was done that has resulted in the present study, no critical examination was made of the fossil plants, hence this erroneous assumption remained unchallenged.

In 1907 Mr. W. T. Lee* began a study of the coal in the Raton field, and while prosecuting this work he discovered the presence of an unconformity in the midst of the section of coal-bearing, supposed Laramie rocks. This unconformity was traced throughout the entire Raton Mesa and subsequently was carried around the southern end of the mountains and well up along their west front.† The rocks below the unconformity, to which the name Vermejo formation has been given, have a maximum thickness of only about 375 feet, while the rocks above the unconformity, now called the Raton‡ formation, are about 1600 feet in thickness. In some places the Raton formation rests on the full thickness of the Vermejo formation, while in other localities the Vermejo is greatly reduced, and in at least one place the entire Vermejo, together with the underlying Trinidad sandstone, has been removed and the Raton rests directly on Pierre.

When the unconformity had been demonstrated it became of the greatest interest and importance that the fossil plants should be studied to ascertain their bearing, first on the distinctness of these two formations, and second, as to their bearing on the question of age. The present study was undertaken to furnish such answers as it might to these two questions. The writer has been fortunate in having at his disposal the original

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* Bull. Geol. Soc. Am., vol. xx, pp. 28–30, 1909.

† Bull. Geol. Soc. Am., vol. xxiii, pp. 571–686, 1912.

‡ *Raton formation* is the name recently adopted by the U. S. Geological Survey for the coal-bearing rocks above the unconformity in the Raton Mesa region of southern Colorado and northern New Mexico. Those below the unconformity have been named *Vermejo formation.* The two constitute what has heretofore been called Laramie in this region. The data upon which they were separated are contained in a forthcoming paper on the Raton Mesa region by F. H. Knowlton and W. T. Lee, which will be published by the U. S. Geological Survey.

material studied by both Lesquereux and Newberry, together with splendid recent collections brought together by Lee, Richardson, St. John, and others, the whole making, perhaps, the largest and most complete collection ever assembled for any Rocky Mountain area. The results of this study are seemingly conclusive.

The full discussion of this flora from the biological standpoint, together with diagnoses and illustrations of the species, will appear in a report by Lee and Knowlton now in preparation. This report is so far completed as to permit the following statement to be made:

The total flora of the Raton Mesa region comprises 257 forms, of which number 106 belong to the lower, or Vermejo and Trinidad formations, and 151 to the upper, or Raton formation. Only 4 species have been found to cross the line of the unconformity, which is taken as pretty conclusive evidence of the distinctness of these two formations.

Taking now the flora of the Vermejo formation, with its total of 106 species, it is natural first to compare it with the Laramie of the Denver Basin. It is found, however, that there is only one species in common to the two areas, which is negligible when it is recalled that the Laramie flora comprises about 97 species, and, as stated above, the Vermejo 106 species. The Laramie of the Colorado Springs area has three or four species common to the Vermejo flora, but even this number is too small to be of importance.

The Vermejo flora is found to have an intimate relation with the Mesaverde (Montana) on the west side of the mountains, in fact, it is demonstrated that about 90 per cent of this flora enjoying an outside distribution occurs either in the original Mesaverde near Durango, Colorado, and its stratigraphic equivalents within this area, or in beds of similar age at Point of Rocks, and the Laramie Plains, Wyoming, at Coalville, Utah, etc. Therefore, the Vermejo flora is regarded as being of Montana age and in the approximate position of the Mesaverde.

The Raton formation, that is, the beds above the unconformity, may now be considered. Of its 151 species only 5 are found to be common to the Laramie of the Denver Basin, which shows that this relationship is remote. With the Arapahoe there are 4 species in common with the Raton flora, all of them occurring also in the overlying Denver formation. With the flora of the Denver formation, however, the relation is very different, for of its 98 described species about 40 are found in the Raton flora. This means that over 40 per cent of the described Denver flora is found also in the Raton flora, and when the large collection accumulated in recent years from the Denver are worked up this percentage will undoubtedly be considerably increased.

As already mentioned, Lesquereux noted the evident affinity of the flora here called the Raton flora with that of the "Lignitic" or "Eo-lignitic" of Mississippi. These beds are now known as the Wilcox formation, which extends from Western Georgia through Alabama, Mississippi, Louisiana, and well into Texas. It rests conformably on the marine Eocene Midway formation, and has at various points intercalated beds of marine Eocene invertebrates, hence there can be no doubt as to its age. The flora of the Wilcox formation comprises, as at present standing in the books, about 65 species, but Mr. E. W. Berry has recently secured large additional collections and has prepared a monograph in which he has enumerated about 170 species, many, however, from the upper portion of the formation. Over 30 species of plants are common between the Raton and Wilcox formations and the conclusion is reached that the Raton formation is to be correlated with the Wilcox and is also Eocene in age.

As it has been shown that there is an intimate relation between the Raton and Denver formations, it naturally follows that if the former is Eocene, as now demonstrated, the latter is also to be so regarded. This, however, is simply a confirmation of the original contention of Cross,* when he described and named the Denver formation in 1889, and in his latest published utterance he again insists on this view. In the latter paper he says†: "I desire now to urge their reference [the Shoshone group] to the Eocene. The Denver beds were originally referred by me to the Eocene, but the great weight attached to the Mesozoic affinities of the vertebrate fauna by paleontologists led to a tentative acquiescence in the assignment of the Arapahoe and Denver formations to Cretaceous in the Denver monograph." All the direct and collateral observations recently made within this area have confirmed this reference to the Eocene.

The wider application of the results here recorded to the stratigraphic position of certain ceratopsian dinosaurs as reported from many other localities, is obvious, since if the Denver is Eocene and is older than the Lance formation, as it is now believed to be, it naturally follows that the latter is the more certainly Tertiary.

Summary.

(1) The coal-bearing section of the Raton Mesa region of Colorado and New Mexico was at first (1867 to about 1883) considered to be of Tertiary age, but later (1883–1905) it came

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* The Denver Tertiary Formation, this Journal (3), vol. xxxvii, pp. 261-282, 1889.

† Proc. Wash. Acad. Sci., vol. xi, p. 42, 1909.

to be regarded as Cretaceous (Laramie) on account of its supposed stratigraphic identity with the Laramie of the Denver Basin.

(2) In 1907 W. T. Lee detected the presence of a widespread unconformity in the midst of this supposedly continuous Cretaceous section, the beds below the unconformity being named the Vermejo formation, and those above the Raton formation.

(3) The distinctness of these formations is abundantly confirmed by the paleobotany, since of the 106 Vermejo species and 151 Raton species only four cross the line of the unconformity.

(4) The Vermejo formation is shown by the plants to be Cretaceous (Montana) in age, being in the approximate position of the Mesaverde.

(5) The Raton formation is shown to be essentially of the same geologic age as the Denver formation of the Denver Basin, and of the Wilcox formation of the Gulf region, the latter being indisputably of Eocene age.

(6) The conclusion is therefore reached that the Raton and Denver formations are Eocene in age, a confirmation of the original contention of Cross as to the Denver.

Art. XLV.—*Recent Discovery of Dinosaurs in the Tertiary*;[*] by W. T. Lee.

The fossils forming the subject of this paper were found about nine miles east of Colorado Springs, Colorado, south of Jimmy Camp Creek, in sec. 3, T. 14S., R. 65 W., about 500 feet above the base of the Dawson arkose (the lower part of the Monument Creek formation of former writers). Geologists since the time of Hayden have referred these beds to the Tertiary, and Richardson[†] has recently added much to our knowledge of them, strengthening their reference to the Tertiary by showing that they are conspicuously unconformable with the Laramie and that they contain a large flora which, according to Knowlton, is essentially the same as that of the Raton formation[‡] or the oldest Tertiary of the Raton Mesa region and with that of the Eocene Wilcox formation of the Gulf Coast. Richardson has also shown to the satisfaction of many geologists that the lower part of the Monument Creek, which he has called *Dawson arkose*, is the stratigraphic equivalent of the Denver and Arapahoe formations of the Denver Basin. This equivalency is confirmed by the fossil plants, inasmuch as those from the Dawson arkose belong to the Denver flora. The subject will be presented by Richardson more fully in the Castle Rock folio, now in course of preparation.

Geologists will recall that the Denver and Arapahoe formations have long been known to contain the Ceratopsian dinosaurs which originally furnished the grounds for retaining these formations in the Cretaceous even though they were known to contain an Eocene flora and to be separated from the underlying Cretaceous by an unconformity that, according to Emmons,[§] marks "unquestionably one of the most important events in the orographical history of the entire Cordilleran system." Some geologists did not agree with this disposition of the formations but were overruled, and Cross[‖] has recently

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[*] Published by permission of the Director U. S. Geological Survey.

[†] Richardson, G. B.: The Monument Creek group, Geol. Soc. America, Bull., vol. xxiii, pp. 267–276, 1912.

[‡] *Raton formation* is the name recently adopted by the U. S. Geological Survey for the coal-bearing rocks above the unconformity in the Raton Mesa region of southern Colorado and northern New Mexico. Those below the unconformity have been named *Vermejo formation*. The two constitute what has heretofore been called Laramie in this region. The data upon which they were separated are contained in a forthcoming paper by W. T. Lee and F. H. Knowlton, on the Raton Mesa Region, which will be published by the U. S. Geological Survey.

[§] Emmons, S. F.: Orographic Movements in the Rocky Mountains, Geol. Soc. Amer., Bull., vol. i, p. 285, 1890.

[‖] Cross, Whitman: The Laramie formation and the Shoshone group, Washington Acad. Sci., Proc., vol. xi, p. 42, 1909.

reiterated the opinion expressed years ago, that the Denver and related formations are of Tertiary age.

Richardson states in the paper just cited (p. 272) that he found a mammalian bone in the Dawson arkose which, according to Gidley, is characteristically Creodont. Gidley says of it: "From our present knowledge the type represented could not be older than Wasatch." Although the bone was not found in place, there is no reasonable doubt that it weathered from rocks near by, and inasmuch as there is no remnant of a younger formation within many miles of the locality where it was found, it seems certain that it came from the Dawson arkose. This is further emphasized by the fact that the bone has perfectly fresh surfaces and shows no evidence of having been transported. In the same paper (p. 275) Richardson points out the fact that certain dinosaur bones collected by Marsh many years ago in Monument Park, north of Colorado Springs, must have come from the Dawson arkose, but these bones seem to have been lost.

During the past summer (1912) the writer had the opportunity of visiting the locality where the Creodont bone was found and there collected the remains of turtles and of dinosaurs. The turtles were examined by Dr. O. P. Hay and the dinosaurs by C. W. Gilmore. In his report on the fossils Mr. Gilmore says: "The collection consists of fragmentary Ceratopsian bones, none of which is sufficiently characteristic to determine the genus to which it belongs, and one ungual phalanx is doubtfully regarded as pertaining to the dinosaur Trachodon. Two small shell fragments show the presence of hard and soft shell turtles. Of these Dr. Hay says, 'the soft shell resembles those of the Lance formation; the other resembles those from the Wasatch but is too fragmentary to be certain of its affinities.'"

We have then at this locality, near Colorado Springs, in beds that lie unconformably on the Laramie and extend laterally across the eroded edges of older formations to the pre-Cambrian crystallines, a flora that correlates the beds with undoubted Eocene on the one hand, as Knowlton's data given in the accompanying paper show so convincingly, and on the other with the Denver and Arapahoe formations; a mammal of a type not known heretofore to be older than Wasatch; one turtle whose nearest known allies are in the Wasatch fauna; another that resembles those of the Lance fauna; and dinosaurs that have been somewhat generally regarded as indicative of Cretaceous age but which occur in associations that convince some geologists that they are Tertiary. Considering this association of fossils in connection with the great unconformity, it seems wholly irrational longer to regard a formation as Cretaceous merely because it contains dinosaurs. To some geologists it seemed equally irrational years ago to refer the Denver and Arapahoe formations to the Cretaceous purely on the basis of the dinosaurian remains. It is possible that a few will still insist that because of the presence of Ceratopsian dinosaurs, the Dawson should be referred to the Cretaceous in spite of its stratigraphic relations, in spite of its other vertebrate remains, and in spite of the evidence of its fossil flora, but the writer ventures to hope that better counsel will prevail. Because of this possibility it may not be out of place in this connection to recall that Gardner* found dinosaurs of the typical "Ceratops beds" fauna in beds lying "unconformably above the 'Laramie' and below the Wasatch" at Ojo Alama in northwestern New Mexico, and also in rocks in similar position near Dulce, New Mexico, and that Lee† also found a dinosaur near Durango, Colorado, in beds supposed to be of the same age.‡ It seems probable, therefore, that in the southern part of the Rocky Mountain region some of the dinosaurs occur normally above a great unconformity, as they do in so many places in the northern part, and that this unconformity may be general thoughout the Rocky Mountain region. These recent finds tend to confirm Knowlton's§ statement that the fauna represented by Triceratops and its associates is found only above an unconformity.

Whether a certain formation shall be regarded as Cretaceous or Tertiary is largely a matter of definition, and there seems to be little hope of unanimity of opinion as to where the line of separation between these two systems should be drawn in the Rocky Mountain region. But in the light of recently acquired information the statement made by Chamberlin and Salisbury‖ regarding the age of the Denver and Arapahoe formations applies at the present time, with increased force, not only to these but to the Dawson and other Triceratops-bearing beds, namely: "If the presence of saurian fossils demonstrates the Cretaceous age of the beds containing them, the Arapahoe and Denver beds are Cretaceous; but every other consideration seems to point to their reference to early Tertiary."

Heretofore the principal argument for including the dinosaur-bearing formations in the Cretaceous has been the presence of the dinosaurs, but this argument is now invalidated by the presence

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* Gardner, James H.: The Puerco and Torrejon formations of the Nacimiento group, Jour. Geology, vol. xviii, p. 734, 1910. See also Brown, Barnum: The Cretaceous Ojo Alamo beds of New Mexico with description of the new dinosaur genus *Kritosaurus*, Am. Mus. Nat. Hist., Bull., vol. 28, pp. 267–274, 1910.

† Lee, W. T.: Stratigraphy of the coal fields of northern central New Mexico, Geol. Soc. America, Bull., vol. xxiii, p. 619, 1912.

‡ Op. cit., p. 592.

§ Knowlton, F. H.: Where are the Laramie dinosaurs? Science, new ser., vol. xxxiv, p. 319, 1911.

‖ Chamberlin, T. C., and Salisbury, R. D.: Textbook, vol. iii, p. 158, 1906.

of Ceratopian remains and a Tertiary mammal in the same formation (Dawson). Messrs. J. W. Gidley and C. W. Gilmore have called the writer's attention to a similar occurrence in Patagonia, where, according to these authorities, "there is a commingling* of dinosaurs with mammals which are apparently of undoubted Tertiary age." But F. B. Loomis,† who has collected from some of these beds, doubts the contemporaneity of the dinosaurs and the mammals. However, Sinclair‡ says of them "It seems to be positively established that dinosaurs and mammals occur in the Notostylops beds. The mammals are not like those known elsewhere from the Cretaceous but are of highly advanced type comparable to those of the Puerco Paleocene of North America. Either we must admit that dinosaurs existed during the Tertiary in South America or change our ideas regarding Cretaceous mammalian types." The recent examination of the structural relations of the Dawson arkose to the underlying beds, as well as the fossil plants and mammal, tends to establish its Tertiary age and to necessitate the acknowledgment that Ceratopsian dinosaurs existed in the Rocky Mountain region in early Tertiary time.

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* Ameghino, Florentino: Les formations sedimentaires du Cretace superieur et du Tertiaire de Patagonie: Museo Nacional de Buenos Aires, Anals, vol. xv, ser. 3, viii, 1906.

Also, Roth, Santiago: Beitrag zur Gliederung der Sedimentablagerungen in Patagonien und der Pampas region, Neues Jahrbuch, Beilage Band xxvi, pp. 92–150, 1908.

† Personal communication.

‡ Sinclair, William J.: Contributions to geologic theory and methods by American workers in vertebrate paleontology, Geol. Soc. America, Bull., vol. 23, No. 2, p. 263, 1912.

Art. XLVI.—*Some Variations in Two Common Laboratory Experiments;* by H. W. Farwell and W. W. Stifler.

1. *A Simple Form of Hot Wire Ammeter.*

An electric current passing through a wire develops in the wire heat at the rate of I^2R watts. If the wire is enclosed in a perfect heat insulator it will of course rise in temperature with the time. Ordinarily, however, it will attain a steady state in a short time if conditions outside are maintained constant, and in this steady state will lose heat to its surroundings at the same rate as it is received. Suppose the wire to be surrounded by, but not in contact with, a good heat conductor with large heat capacity. This will give the same conditions as those to which Newton's law of cooling may be applied, provided the wire is not raised to a temperature greatly different from that of the surrounding heat conductor. It will lose heat then at a rate equal to $K(T_1-T_0)$ where T_1 is the temperature of the wire and T_0 is that of the heat conductor and K is a constant depending on the material and nature of the surface of the wire. In the steady state then

$$I^2R = JK(T_1 - T_0)$$

where J is the mechanical equivalent of heat.

If the wire has at the temperature of the surroundings a length L it will have at temperature T_1 a length

$$L + \Delta L = L[1 + \alpha(T_1 - T_0)]$$

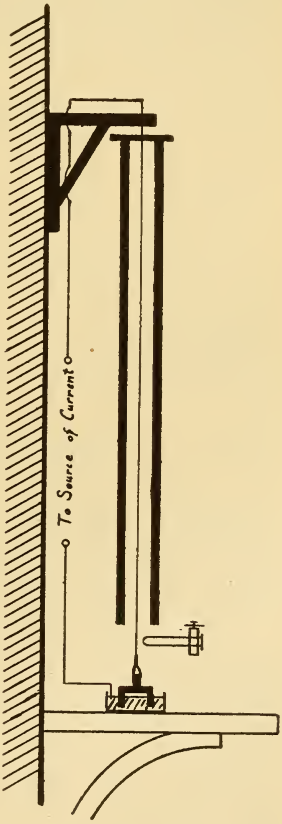
where α is the coefficient of expansion of the wire. Or

$\Delta L = L\alpha(T_1 - T_0)$. That is

$$I^2R = \frac{JK\Delta L}{L\alpha} \text{ or } \Delta L = \frac{I^2RL\alpha}{JK} = c \cdot I^2$$

That ΔL may be large a long wire of small cross-section of a material with a large coefficient of thermal expansion would be necessary.

Fig. 1.

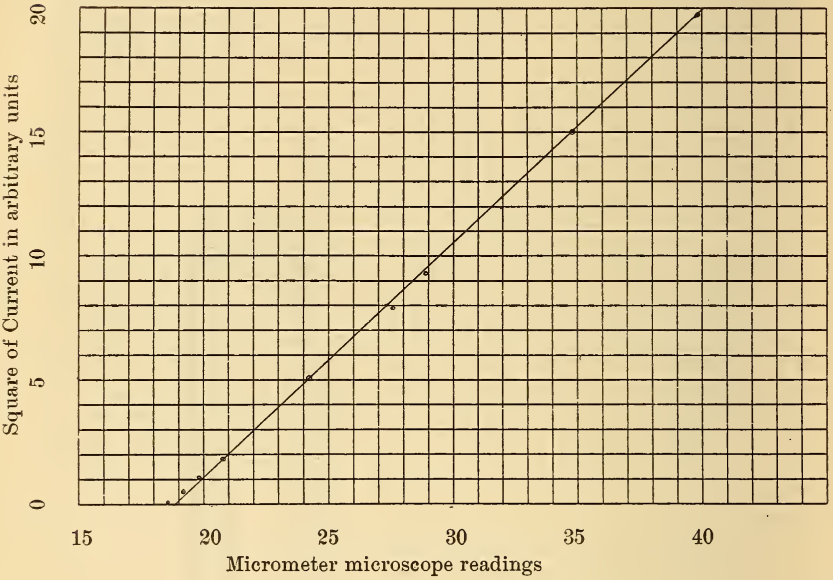


These conditions are usually found in the apparatus used in every laboratory for the measurement of Young's modulus.

This apparatus may readily be converted into a fairly satisfactory hot wire ammeter, merely by connecting the ends of the wire to the circuit. A desirable feature is the addition of a heavy metal tube to enclose the wire.

As set up for purposes of demonstration in our laboratory the apparatus consisted of a piece of No. 30 B. & S. brass wire about 130^{cm} long, connected to the circuit by means of the support at the top, and at the bottom through a mercury cup in which hung a small weight attached to the wire. The weight served to keep the wire straight and under uniform tension, while the mercury served for the double purpose of making contact and damping any pendulum motion. The wire was surrounded for its whole length by a heavy piece of gas pipe, closed at the top. The increase in length was observed by a micrometer microscope. The curve above gives the results of one set of observations taken by one of our students, the current range being from ·15 to 1·12 amperes.

Fig. 2.



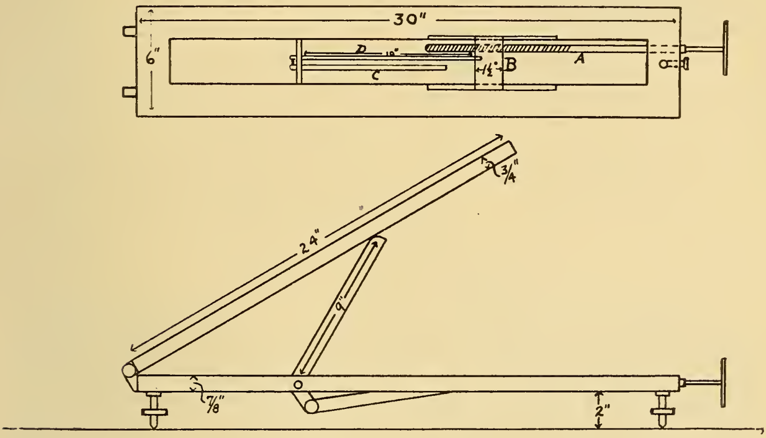
Observation of the time required for the wire to return to its original length would make the method available for the determination of the mean coefficient of linear expansion of metal in the form of wire, though probably not with any degree of accuracy.

2. *An Improved Inclined Plane.*

The unsatisfactory results obtained in our laboratory with various inclined planes and friction planes have led to the construction of a form of plane which may be of some interest to those who have experienced the same difficulties.

The chief sources of trouble appeared to be in lack of rigidity, uncertainty of angular motion, and lack of fine adjustment. These are all of a mechanical nature, and have been practically eliminated by our mechanician, Mr. Cooey. The plane and its bed are of cast iron and are machined to a satisfactory finish. The upper surface of the plane has been carefully planed, and polished to some extent, though not as much as possible. The bed is furnished with levelling screws. The hinge is formed by accurately boring openings in the tabs on the two castings and closing them with drill rod pins. To avoid unnecessary weight, both bed and plane are much thinner in the middle than at the edges, the dimensions given in the figure referring to the *outside* measurements.

Fig. 3.



The elevating device is attached to the inside of the base. Its operation may be readily understood by reference to the diagrams. The inside of the base frame is slotted for a short distance near the rear so as to support a rectangular carriage B which is moved forward or backward by means of a screw A which carries a small wheel at its outer end. D is a rod connecting the carriage B with the short arm of the bent lever C. The end of the long arm of C is in contact with the under side of the plane, sliding along on a planed surface as the plane is lifted. As B is moved away from the hinge the plane is steadily raised, and will rest securely in any position. The screw and lever system operates easily, a weight of 30 pounds or more on the end of the plane having been lifted with little effort.

The annoyance of the usual arc for measuring the angles is avoided by using a steel scale to determine the height of the plane. In determinations of the angle of repose the plane is very easily operated, and the adjustments can be made quickly from any position. The iron base permits the attachment of pulleys or other devices without in any way interfering with the operation of the plane.

Columbia University,
Jan. 15, 1913.

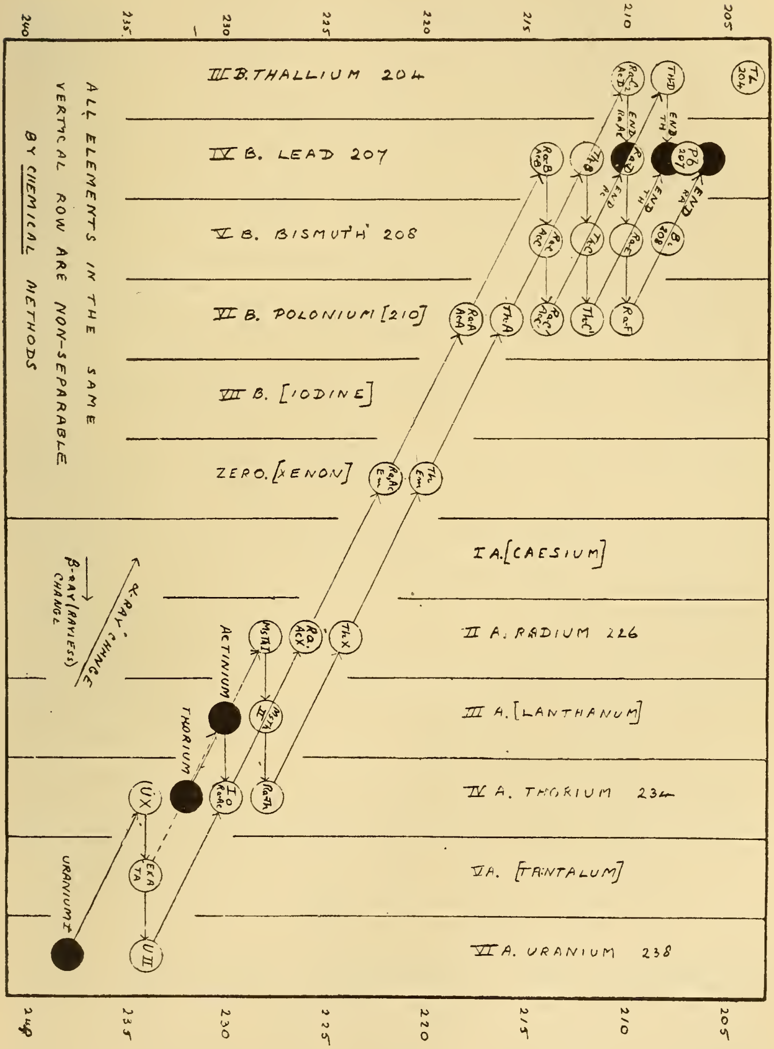
SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *Radio-elements and the Periodic Law.*—Frederick Soddy, some time ago, pointed out that in several cases when the α-particle was expelled the atom passed from a family of even number in the periodic table to the next lower numbered even family, the family of odd number being always missed. Further, in the changes in which the α-particle was not expelled the atom in several cases reverted to its original group, resulting in a curious alternation of properties as the series proceeds. Now, when this occurs, an element of the fourth family, for example, expelling an α-particle and becoming a member of the second family, which after further changes reverts to the fourth family, the two representatives of the fourth family so resulting are not merely similar in chemical properties, but although one of them has lost an α-particle (helium) and has its atomic weight diminished by four units, they are non-separable by any known process. This applies not only to the disintegration products of a single series, but to all the products. Thus, in the fourth group, thorium, uranium X, ionium, radio-thorium, and radio-actinium are all chemically non-separable, though they result from three separate series, and the calculated atomic weight varies from 234 to 228.

A corollary to Soddy's rule for radio-active changes has been advanced by A. S. Russell. This states that when a β-ray or rayless change occurs the atom passes into the family of the periodic table next higher in number, that is, the change in these

RADIO-ELEMENTS AND THE PERIODIC LAW; BY FREDERICK SODDY.



From the *Chemical News*, Feb. 28, 1913.

cases is always from an even to an odd, or from an odd to an even numbered family. It is to be observed that these changes are in a direction opposite to the α-particle changes, and that two of them are required for a return to the original family.

A systematic investigation of the chemical nature of as many of the radio-elements as possible has been made in Soddy's laboratory by Alexander Fleck, with the result that it is now possible to state or to predict the chemical nature of every known member of the disintegration series. Soddy has constructed a diagram of these changes which is here reproduced. He says that these results prove that almost every vacant place in the periodic table between thallium (204) and uranium (238) is crowded with non-separable elements of atomic weights varying several units, and this leads inevitably to the presumption that the same may be true in other parts of the table. It may be predicted that all the end products, probably six in number, of the three series, with calculated atomic weights varying from 210 to 206 should be non-separable from lead, that is, that they should *be* lead, for which the atomic weight 207·1 is now accepted. Nothing further is necessary to explain the failure to obtain numerical relations between the atomic weights, for, accepting this idea, we may consider the elements to be composed of atoms of varying weights of which our atomic weights are averages. It should be observed that the non-separable elements appear to show no differences in their spectra. Soddy suggests the desirability of testing the constancy of the atomic weight of lead from a variety of radio-active minerals.—*Chem. News*, cvii, 97. H. L. W.

2. *Determination of Alkalies in Rocks.*—Y. Krishnayya has described a modification of the usual hydrofluoric acid method for the determination of potassium and sodium in rocks, which appears to be a decided improvement. He decomposes the material with hydrofluoric and sulphuric acids and evaporates off both of the acids. The residue is boiled with hydrochloric acid and if any insoluble matter is found it is filtered off and the treatment is repeated. The whole solution is then made up to a definite volume and a portion of the liquid corresponding to 1 g. of the mineral is evaporated to dryness in a platinum dish which is then ignited over a free flame until fumes of sulphuric acid cease to come off. As the alkalies are in the form of sulphates there is no danger of loss by volatilization. The residue, which comes away easily from the dish and can be readily broken up with a glass rod, is boiled for a minute or two with a little water, and, without filtering, a precipitation is made with barium chloride and an excess of barium hydroxide. After filtering and washing, the solution is treated in the usual way, barium being removed by ammonium carbonate, and the alkalies are weighed together as chlorides. Two test analyses are given which show very satisfactory results. The process appears to be no more laborious than the method of J. Lawrence Smith, while it has the advantage that the complete decomposition of the mineral may be assured.—*Chem. News*, cvii, 100. H. L. W.

3. *Allen's Commercial Organic Analysis;* edited by W. A. Davis and Samuel S. Sadtler. Volume VII. 8vo, pp. 563. Philadelphia, 1913 (P. Blakiston's Son & Co. Price $5.00).—The present volume of the entirely re-written fourth edition of this important work deals with the vegetable alkaloids (continued), glucosides, non-glucosidal bitter principles, animal bases including ptomaines, animal acids, lactic acid, cyanogen and its derivatives. The contributors, of whom four belong in England and three in the United States, appear to have maintained the high standard of excellence of the preceding volumes. H. L. W.

4. *A Foundation Course in Chemistry for Students of Agriculture and Technology;* by J. W. Dodgson and J. A. Murray. 12mo, pp. 244. London, 1913 (Longmans, Green & Co. Price $1.10).—This small textbook presents a short course in elementary chemistry in which the simpler fundamental principles and the more important facts appear to be very well presented. About 75 pages are devoted to organic compounds. There is appended to the book a rather extensive list of well-chosen questions, including a few good examples for calculation. H. L. W.

5. *Osmotic Pressure:* by Alexander Findlay. 8vo, pp. 84. London, 1913 (Longmans, Green & Co. Price $1.00 net).—This is one of a series of monographs on inorganic and physical chemistry, edited by the author of the one under consideration, which are designed to place before advanced students of chemistry certain sections of the subject in a comprehensive manner, with particular attention to recent investigations. The present volume treats its subject in a very able manner, and it is to be recommended to those who are interested in this important field of investigation. H. L. W.

6. *The Possibility of Molecular Agitation at the Absolute Zero.*—Two formulæ have been given by Planck for the energy of a resonator. The second formula differs from the first by the addition of the term $\frac{h\nu}{2}$. If the curves representing these two expressions are plotted on the same diagram with energy (ordinates) as a function of the absolute temperature (abscissæ) it becomes clear that the first curve starts at the origin and always remains below the straight line $E = kT$. This is consistent with the classical theory. On the other hand, the second curve begins with the ordinate $\frac{h\nu}{2}$ at the absolute zero, and becomes asymptotic to the above-mentioned straight line when the temperature, T, approaches infinity. Thus the resonator would have an amount of energy given by $\frac{h\nu}{2}$ at the absolute zero. This result is in contradiction to the classical theory. The differential coefficient of the energy with respect to the temperature, that is, the specific heat, is the same for both of Planck's formulæ.

Starting with these considerations, A. Einstein and O. Stern have been able to compare certain theoretical loci with the curve obtained from experimental data, by Eucken, for the specific heat of hydrogen at very low temperatures. It is shown that "Eucken's results for the specific heat of hydrogen make the existence of an amount of energy $\frac{h\nu}{2}$, at the absolute zero, probable." Furthermore, the authors show that "The hypothesis of energy at the absolute zero opens a way for deriving Planck's radiation formula without the introduction of any kind of discontinuity whatsoever." "It appears doubtful, however, whether the remaining difficulties can be overcome without the assumption of quanta."—*Ann. d. Phys.*, No. 3, March 1913, p. 551.

H. S. U.

7. *The Electric Carbon Arc at Low Pressures.*—The recent investigation of the carbon arc at pressures less than one atmosphere by M. La Rosa has brought to light some interesting facts. The lamp consisted essentially of two inclined carbon rods enclosed in a large glass bell-jar. The distance between the poles was controlled by an automatic regulator. When the air pressure in the jar was decreased to a few centimeters of mercury the arc showed no remarkable changes either electrically or optically. The current remained practically constant, the voltage across the arc decreased slightly, and the length of the arc increased, thus showing that the current passed more readily as the pressure was lowered. The spectrum showed a decrease in the intensity of the second group of cyanogen bands. On the other hand, when the pressure was reduced to a few millimeters the arc gradually changed its essential form and appearance. The core, formed by the anode and cathode flames, and the mantle no longer possessed sharply defined boundaries. The mantle became almost invisible while the core altered to a diffuse luminous region in which various bright and dark parts could be seen. On the whole, the arc at low pressures possessed the well-known characteristics of the discharges in vacuum-tubes. Although the arc changes gradually from the one "régime" to the other as the gas pressure is varied, the investigator convinced himself of the existence of two distinct régimes by the following test: At 5^{mms} pressure and with a resistance of about 19 ohms in the line the current was 5·1 amperes, the drop across the arc was 53 volts, and the length of the arc was 14^{mms}. When the series resistance was increased to about 22 ohms the arc changed abruptly to the usual type, while the current, the voltage drop, and the arc length assumed the values 5·3 amperes, 34 volts, and 2^{mms} respectively. This process was completely reversible.

The spectrum of the arc at low gas pressures (2d régime) differed from that at higher pressures (1st régime) in two general respects: (a) in the distribution of intensities of the various component parts of the spectrum, and (b) in the presence of elements which do not occur in the ordinary arc. Thus, although the carbon bands seem to remain unchanged, the cyanogen bands nearly disappear. Moreover, the bands of this compound are not influenced to the same degree. The second group sensibly vanishes while the regions near the heads of the third and fourth groups remain visible on the photographic negatives. In like manner, only the strongest lines of the metallic impurities of the electrodes persist. For example, only D for sodium, and g, H and K for calcium. The most striking peculiarity of the spectrum at a few millimeters pressure consisted in the occurrence of bands which are usually ascribed to compounds of carbon with hydrogen. Although these bands have been often observed in the spectra of flames and of certain high frequency discharges, it is the first time that they have been found in the carbon arc. At pressures of a few millimeters the lines α, β, and γ of the first spectrum of hydrogen also came out with greater intensity than the lines of any other element. At higher pressures, between 1^{cm} and 2^{cms}, the hydrocarbon bands could still be observed, but the hydrogen lines had sensibly disappeared. The presence of the hydrogen lines supports the current view that the bands are due to compounds of carbon with hydrogen. La Rosa tried in vain to repress the hydrogen lines by removing all traces of water vapor from the air surrounding the arc, by heating the carbons during the air washing, etc. He concludes that the hydrogen is necessary for the production of the bands, and that this element gets into the electrodes in hydrocarbons during the process of manufacture. The preceding phenomena are very sensitive to changes in the pressure of the gases in which the arc burns. In other words, the arc at 2^{cms} differs spectroscopically from the arc at 1^{cm}, and the latter in turn is unlike the arc at 5^{mms} pressure. On the contrary, the amperage and voltage seem to experience no corresponding variations and are certainly not at all sensitive criteria for the nature of the arc. Finally, the investigator showed experimentally that the above mentioned spectral changes are not due to alterations in the composition of the surroundings of the arc.—*Ann. d. Phys.*, No. 3, March 1913, p. 542.

H. S. U.

8. *The Fitness of the Environment;* by LAWRENCE J. HENDERSON. Pp. xv, 317. New York, 1913 (The Macmillan Co.).—This text is an inquiry into the biological significance of the properties of matter. The old belief that natural selection is, on the whole, quite adequate to account for biological fitness is shown to be incomplete and fallacious. Emphasis is laid on the *reciprocal* character of Darwinian fitness. The subject is approached from the point of view of physical chemistry and the ultimate problem is concisely stated as follows: "In what degree are the physical, chemical, and general meteorological characteristics of water and carbon dioxide and of the compounds of carbon, hydrogen, and oxygen favorable to a mechanism which must be physically, chemically, and physiologically complex, which must be itself well-regulated in a well-regulated environment, and which must carry on an active exchange of matter and energy with that environment?" This problem is solved so completely as to show not

only that water, carbon dioxide and organic compounds have the necessary properties to make up a suitable environment for living organisms as we know them, but also that the properties of these substances are practically sufficient, in the sense that no other elements with their compounds can maintain a proper environment in a steady state. The author's style is so simple and clear that the volume combines the entertaining advantages of a novel with the instructiveness and rigor of a thoroughly scientific text. H. S. U.

9. *An Introduction to the Mathematical Theory of Heat Conduction;* by L. R. Ingersoll and O. J. Zobel. Pp. vi, 171, 24 figures. New York, 1913 (Ginn & Co.).—The aim of the authors has been twofold: (a) to develop the subject with special reference to the needs of the student who has neither time nor mathematical preparation to pursue the study at great length, and (b) to point out more clearly and specifically than usual the many applications of which the theoretical results are susceptible. Hence, the text may be used to advantage as the basis of a first course in mathematical physics. The practical applications will also be interesting to geologists and engineers because they include such questions as the cooling of the earth with and without radioactive influences, the cooling of lava under water, the tempering of steel, the freezing of concrete, electric welding, fireproof walls, etc. The usefulness of the volume is increased both by the 61 problems for solution by the student and by the six appendices of thermal data and mathematical formulæ and tables. H. S. U.

10. *Elements of the Precision of Measurements and Graphical Methods;* by H. M. Goodwin. Pp. 104. New York, 1913 (McGraw-Hill Book Co.).—This book is an amplified presentation of the printed "Notes" which the author has used for a number of years in connection with his laboratory classes in the Massachusetts Institute of Technology. The degree of advancement of the text may be inferred from the fact that the subject is introduced about the middle of the sophomore year, as soon as the students have performed six or eight experiments on fundamental measurements in Mechanics and can handle the elements of the Differential Calculus.

Part I, pages 7 to 38, deals with the precision of measurements; Part II, pages 41 to 56, relates to graphical methods; and Part III, pages 69 to 98, comprises the solutions of a few illustrative problems together with a list of 79 unsolved questions and problems to be discussed by the student. The appendix includes tables of selected mathematical constants, approximation formulæ, squares, cubes, reciprocals, four-place logarithms, and natural and logarithmic sines, cosines and tangents. The treatment is so very clear and concise, and the material is so wisely chosen that the volume deserves serious consideration by all who are engaged in teaching laboratory classes in college-grade physics. H. S. U.

11. *Electricity* (Home University Library); by Gisbert Kapp. Pp. v, 256, 26 figures. New York (Henry Holt & Co.).—In this

little 16mo volume the author presents in an elementary and semipopular style the fundamental phenomena and laws of static and current electricity. The practical applications to direct and alternating current dynamos and to the problem of power transmission are discussed at some length. Although, in general, the text seems to be as accurate as is consistent with its scope and elementary nature, nevertheless some of the definitions might have been made to conform more closely to scientific rigor. For example, on page 19, the dyne is defined as " . . . that force which, acting steadily in the same direction for a second on the mass of one gram, will give it an acceleration of one cm. per second per second." H. S. U.

12. *Elementary Principles of Electricity and Magnetism for Students in Engineering;* by ROBERT HARRISON HOUGH and WALTER MARTINUS BOEHM. Pp. vii, 233, with 95 figures. New York, 1913 (The Macmillan Co.).—"The object of this text is to develop, in logical order, the more important numerical relations existing among the principal quantities employed in electricity and magnetism." "Only those relations which are fundamental to the design of the various machines and instruments used in engineering practice are developed." All of these formulæ, 668 in number, are collected in a single table immediately preceding the index. A knowledge of mechanics and trigonometry should precede, but analytic geometry and calculus may accompany, the study of this course. Problems, for solution by the student, are collected at the ends of some of the chapters. The numbering of these exercises from 1 to 152 may be deceptive because several gaps exist in the list. In more than one noteworthy instance the authors have substituted their own notation, for certain electrical and magnetic quantities, in place of the accepted and classical symbols. For example, β is used to denote magnetic induction instead of B, etc. H. S. U.

13. *Methods of Measuring Electrical Resistance;* by EDWIN F. NORTHRUP. Pp. xiii, 389, with 162 figures. New York, 1912 (McGraw-Hill Book Co.).—Since the author has been engaged in electrical measurement for over twenty years and was formerly connected with the Leeds and Northrup Company of Philadelphia for more than seven years, the expectation of an authoritative treatise from his pen is immediately aroused. On careful examination of the text it is found that the most sanguine hopes of the reader are realized and perhaps even exceeded. Some of the methods are new and are described for the first time. Northrup says in the preface: "While it is not claimed that the work is exhaustive, the author has selected for presentation all methods which in his judgment are useful, for commercial tests and measurements, for purposes of instruction in educational institutions and for application in technical and research laboratories."

It seems desirable to show the scope of the volume by giving the headings of some of the chapters, such as: I "Extent, Character and Precision of Electrical Measurement. Theory of

Errors. Ohmic Resistance," III "Null Methods. Resistance Measured by Differential Instruments," V "Wheatstone-bridge Methods. Variable Rheostat. Arrangements of Resistances. Per Cent Bridge. Suggestions for Using Bridge," VII "The Determination of Electrical Conductivity," IX "Insulation Resistance of Cables," X "Resistance as Determined with Alternating Current," XI "Resistance Measurements when the Resistance Includes an Electromotive Force," XII "Elementary Principles of Fault Location," XIII "Measurement of Temperature by the Measurement of Resistance," and XV "Deflection Instruments and Galvanometers." The appendix contains much useful material. Finally, a novel feature of the composition of the book consists in numbering the articles of each chapter with the same multiple of 100 as is the number of the respective chapter. Thus, the articles of Chapter XII are numbered consecutively from 1200 to 1217 inclusive. In like manner the figures have the same numbers as the articles to which they pertain. H. S. U.

14. *Stabilität, Labilität und Pendelungen in der Elektrotechnik*; by HANS BUSCH. Pp. viii, 246, with 69 figures. Leipzig, 1913 (S. Hirzel).—This monograph is a revised and much amplified presentation of the author's doctoral dissertation at the University of Göttingen. As the title partly suggests, the book is chiefly devoted to a discussion of the conditions and criteria for stability, instability, and forced vibrations in dynamos and electric motors of various types. The first three chapters are mainly theoretical while the fourth and last chapter deals with the practical applications of the preceding. H. S. U.

II. GEOLOGY AND MINERALOGY.

1. *The Formation of Coal beds*; by JOHN J. STEVENSON. Pt. III, Proc. Amer. Phil. Soc., vol. li, pp. 423–553, 1912.—In this readable work Professor Stevenson discusses the nature of the rocks of the Coal Measures and their mode of deposition in the northern Appalachian basin. The general stratigraphy and areal distribution of the formations and the irregular deposition of the sediments are treated in the opening part of the work. Then follows a discussion as to the significance of rounded fragments of coal in sandstone, how the sandstones and shales including the red beds were deposited, the nature of the marine and freshwater limestones and the testimony of the fossils as to depth of water. There is a wealth of information here for students of sedimentation and for stratigraphers, to all of whom the paper is commended.

The article tells of the work of mighty rivers, whose valleys were periodically invaded by shallow and narrow seaways, with waters more or less prolific in marine animals. The following are some of the author's conclusions :

"The widespread horizontality of the Coal Measures deposits, coarse and fine alike, recalls conditions observed on the Siberian Steppe and other river regions. The folding of the beds proceeded from a common cause, lateral pressure applied at the east. The violence of plication decreases with notable regularity toward the west, until in western Pennsylvania and in Ohio, along a line of more than 100 miles, the folds become so gentle that they can be traced only by close study. Dips of more than one degree are unusual, while at times and for considerable distances the dip is barely one half of a degree. The same condition exists in a great part of West Virginia. The regular decrease in steepness of the folds leads to the belief that originally the beds were, to all intents, horizontal throughout the basin, the condition being that observed on the great river plains of comparable extent. The rare occurrence of driftwood in the widespread deposits is characteristic not only of the Coal Measures but also of vast river deposits, those of the Amazon, as described by Brown, and of the Ganges as described by Medlicott and Lyell. The long narrow areas of coarse to pebbly sandstone, often with driftwood, recall the filled valleys of the Sierra, described by LeConte, as well as filled deserted bows on the Mississippi and the filled channels so often disclosed when a stream in flood cuts across its 'bottom.' The distinct evidence of sorting of materials in the red shales, where clay and sand are in dovetailing lenses, as well as in some conglomerates, where hardly enough fine material remains to bind the pebbles, leaves little room for doubt that the work was done by streams moving rapidly in some cases, slowly in others. The pebbles are not flat, such as one may find on a shore, but oval or sub-spherical, river pebbles, and their gradual decrease in size as well as number in certain directions shows that the materials were rehandled many times. The rounded pebbles of coal and carbonaceous shale prove equally with those of quartz and sandstone that the deposits, whence they came, cropped out and were exposed to attack by streams of water. The marine limestones, with one exception, are in definite, long, narrow and comparatively insignificant areas, and pass, at the borders, where those remain for observation, into sandstone, chert or shale, the condition being that of an estuary surrounded by lowland, whose rivers bring a minimum of sediment. The shallowness of the water by which sediment was distributed and the short duration of the flooding are disclosed by wave marks, sun cracks and footprints of animals, occurring at so many horizons, while the moderate depth of the estuaries, in which limestone was formed, is apparent from the shore conditions of the limestone. The testimony of the fauna is confirmatory; that life needed not deep water, for it persisted to the very shore line in Ohio. Unconformability by erosion or by overlap marks the contact of Pennsylvanian with the underlying Mississippian in almost the whole basin, showing that the great part was dry land.

"The record appears to show that the Appalachian basin, between the Alps-like Appalachia at the east and the low-lying Cincinnatia at the west, was divided longitudinally by the flat-topped and only moderately high Alleghania. The deepest portion of the eastern valley lay close to the foot of Appalachia, whence the surface rose westward almost imperceptibly to the crest of Alleghania. The western valley extended as a plateau with its low line crossing eastern Ohio in a south-southwest direction and deepening southwardly. . . .

"Each basin had its longitudinal river. That of the east, rising in the present confines of New York, flowed with low gradient for more than 1,000 miles, receiving many tributaries from the bold Appalachia and many, perhaps, unimportant tributaries from the gentle slope at the west. Flowing at first close to Appalachia, it was pressed constantly westward by alluvial fans and cones, which became confluent and finally were modeled into a vast river plain. The main stream was sluggish and often interrupted ; during high floods, the surface was covered broadly by a sheet of water and the débris from different streams was mingled. The river in the western basin received no débris-laden tributaries from east or west, except at the extreme north ; it was more rapid than that in the east and pushed its coarse materials far southward. Progressive overlaps show that subsidence prevailed throughout the basin until the later stages, when it was confined to the contracting area of deposit ; but it was differential and not constant. There were long intervals of slight or no movement during which rivers, reduced to base-level, distributed mostly fine material along their lower reaches. At the close of the Pottsville, the valleys had been filled and Alleghania had become buried ; the whole area of deposit was an irregular marshy plain. But the old drainage systems continued until near the close of the Conemaugh and determined the lines of sea invasion ; they disappeared only with changes in the topography, induced by the forces which were eventually to obliterate the basin. During the whole of the Pennsylvanian, a very great part of the basin was near sea-level. After the close of the Pottsville, few portions of the area of deposition seem to have been more than 300 feet above tide and there is no reason to suppose that any portion was at any time much more than 100 feet below tide" (551-553). C. S.

2. *A synopsis of the Recent and Tertiary freshwater Mollusca of the Californian province, based upon an ontogenetic classification;* by HAROLD HANNIBAL. Proc. Malacological Soc., X, Pt. II, pp. 112–166, Pt. III, pp. 167–211, pls. v–viii, 1912.—A painstaking and detailed study of the freshwater molluscs in the Californian province. The species have all been studied in the light of both their normal and abnormal environment. The abnormal factor is an unusual amount of mineral salt in solution. Brackish waters or lakes in arid regions cause the development of "malleations, plications, or scalarity among the Gastropods, arcuity and roughening among the Pelecypods, and other deviations from the types found under normal circumstances. These

examples have been invariably extreme instances, however; the less striking ones pass unnoticed, since hardly a lake, pond, marsh, slough, stagnant stream, semi-estuary, or enclosed or partially enclosed body of water, contains molluscs which are not more or less subject to these aberrancies. Frequently, particularly in the arid regions of Western North America, these forms have been redescribed as separate species, but in no instance are the characters inherited, though the stock may have passed through a long line of abnormal generations. The progeny under such conditions appear to be unusually liable to become abnormal likewise, but this may be explained on the basis of hereditary susceptibility. . . .

"Forms produced under these circumstances are legion, but appear in every instance not as possessing new characters, but the result of an accentuation of the principal environmental and evolutionary influences which affect the mollusc, hence the term *syntonia*. . . .

"The thickness of the shell normally depends, within limits, on the amount of lime in the water. . . . An accentuation of the evolutionary influences in the Gastropoda may produce an exaggeration of the rest periods, resulting in the development of more or less regular costæ, of the spiral striæ causing malleations, angulations, or keeling, of the inflation of the aperture, . . . an unnatural development of the columnar fold . . . and the production of irregularities of growth. . . . The Pelecypoda appear to be rather less susceptible, but arcuity among the Unioids is generally due to this cause. . . . The only salts which occur widespread or in sufficient abundance to be regarded as probabilities are those of sodium, potassium, calcium, and magnesium. Sodium and potassium salts, known commonly as white and black alkali respectively, are frequently abundant in the arid regions of the west. It has been repeatedly observed that one or the other or both may be present in such abundance as to cover entirely the ground in the vicinity of a pond or stagnant stream while the Mollusca are indifferently normal or affected, and when affected seldom to the degree one would expect if the distortion could be the result of the salt in question. Calcium salts, as is well known, have no deleterious effect upon molluscan life, but are a prime necessity for its existence. Magnesian compounds, on the other hand, produce remarkable physiological effects and act as poisons.

"Reasoning on this basis the writer has undertaken a series of experiments with balanced aquaria which prove beyond doubt that the small quantities of magnesium salts ordinarily present in stagnant water produce these puzzling forms, and once produced, their results are not readily overcome. Both the sulphate and the chloride appear to be equally pernicious.

"Whether or not other salts have similar effects has not been ascertained in every case. The eight or nine commoner ones in ordinary water produce no appreciable distortion" (114–116).

C. S.

3. *Materialien zu einer Monographie der Halobiidae und Monotidae der Trias;* by Ernst Kittl. Extracted from "Resultate der wissenschaftl. Erforschung des Balatonsees," I. Bd., I. Teil, Pal. Bd. II. Pp. 229, 10 pls., 37 text figs., 1912.—Here are described with care a wealth of Triassic bivalves of the families Halobiidæ and Monotidæ. The Paleozoic genus Posidonia is the stem form of the Halobiidæ, out of which in Triassic time developed Daonella, and the stock then gave rise either monophyletically or more probably polyphyletically to Halobia. The new genera *Enteropleura* and *Dipleurites* each have but a single species restricted to the Triassic of Germany. The family Monotidæ has but the one genus Monotis.

Considerable space is also devoted to young and small forms, and to a discussion of how to distinguish them from the phyllopods such as Estheria. C. S.

4. *Das Gesetz der Wüstenbildung in Gegenwart und Vorzeit;* by Johannes Walther. Second edition. Pp. 342, 147 figs. Leipzig, 1912.—The first edition of this interesting and highly instructive book appeared in 1900. Since then the author has again visited Egypt and the Sudan. The present edition is much improved, and is longer and far better illustrated. It is of great import to geologists and glaciologists. In studying ancient glacial climates the author finds it necessary to accept the theory of pole wandering. C. S.

5. *Palaeontologia Universalis*, Fasc. I, Ser. IV, July, 1912.—This part treats of twenty-five old species here redefined. Of American species there are: *Calymene callicephala, C. platys, Asaphus micrurus*, and *Ceraurus pleurexanthemus.* C. S.

6. *Canada Department of Mines.*—Recent publications of the Canada Department of Mines (see vol. xxxiv, p. 487) are as follows:

(1) Geological Survey Branch; R. W. Brock, Director. Summary Report for the calendar year 1911. Pp. x, 412; 7 text figures and 9 diagrams and 2 maps. This is a general account of the work of the year giving an outline of what was accomplished by some forty parties, including six engaged in topographical work.

(2) Mines Branch; Eugene Haanel, Director. Summary Report for the calendar year ending December 31, 1911. Pp. ix, 208; 16 plates, 6 figures, and one map.

General Summary of the Mineral Production of Canada during the calendar year 1911; John McLeish. Pp. 38. Special reports by the same author have also been issued discussing the production in 1911 of cement, clay products, etc.; of iron and steel; of copper, gold, lead, nickel, etc.; of coal and coke.

Preliminary Report on the Mineral Production of Canada during the calendar year 1912; prepared by John McLeish. The total value of the mineral production was $133,127,500, an increase of about $30,000,000, or 29 p. c., over 1911.

An Investigation of the Coals of Canada with reference to their Economic Qualities as conducted at McGill University, Montreal.—Of this important work under the charge of J. B. Porter and R. J. Dudley, to be completed in six volumes, volumes III and IV were added in 1912.

Report on the Building and Ornamental Stones of Canada. Vol. I; by WM. A. PARKS. Pp. xiii, 376; 77 plates.

Pyrites in Canada; Its occurrence, exploitation, dressing, and uses; by ALFRED W. G. WILSON. Pp. xi, 202; 27 plates, 29 figures.

Bulletin No. 8. Investigations of the Peat Bogs and Peat Industry of Canada, 1910–11; by A. ANREP. Pp. viii, 61; 19 plates, 1 figure, and 12 maps (in pocket).

7. *Die Erklärende Beschreibung der Landformen;* by WILLIAM MORRIS DAVIS, edited by Dr. A. RÜHL. Pp. xvii, 565; 212 ills., 13 tables. Leipzig and Berlin, 1912 (B. G. Teubner).—The scope of the present work is indicated by the following chapter headings: The Content of Geography, The Erosion Cycle, Confrontation of Theory with Fact, Development of a Deductive Scheme, Simple Structures, Complicated Structures, Mountains, Volcanic Features, The Arid Cycle, The Glacial Cycle, The Marine Cycle. The matter used was originally presented in a course of lectures delivered in Berlin during the winter term of 1908–09. Much new material has been added particularly in the chapters on deserts, glaciation and shore lines. While the methods of research developed by the author as well as the conclusions drawn are familiar to American geologists. the present book will repay careful reading. It is the best general treatment of Physiography which has so far appeared, and its wealth of pictorial and verbal illustrations adds to its value as a reference text. H. E. G.

8. *Ocean-depth Charts of the Berlin Institut für Meereskunde.*—Three charts of ocean depths, prepared by Dr. Max Groll and issued by the Institut für Meereskunde of the University of Berlin, serve admirably to summarize present knowledge of ocean basins. The charts are on a central scale of 1 : 40,000,000, and are specially projected according to Lambert's true-area device, so as to include the Atlantic, the Pacific and the Indian oceans with their southward extensions. The lands are uniformly tinted in ochre; the shallow continental waters, down to 200 meters, in a lighter shade of the same color; then increasing depths for every 1000 meters are shown in darkening shades of blue down to 6000 meters; after which purple, pink and red show more extreme depths. Several results stand forth clearly; large unexplored areas have contours of simple pattern, evidently because of lack of data rather than because of simplicity of fact. Several lines of soundings from California to Fiji demand much greater irregularity of bottom contours than can now be drawn for the neighboring unexplored spaces. The most striking fact is the occurrence of maximum depths, not in the middle of the ocean basins farthest from the lands, but in narrow troughs, closely associated with the borders of the continents or with

island chains. This peculiarity of distribution is strongly confirmatory of the theory that the troughs represent modern and probably continuing deformation of the ocean bed. W. M. D.

9. *Volcanoes, their Structure and Significance;* by T. G. Bonney. Third edition. Pp. 379; 21 figs., 16 plates. New York, 1912 (G. P. Putnam's Sons).—The popularity and usefulness of this volume is shown by its passage into a third edition. Here are brought together into clear and interesting form the descriptions of volcanoes and their great eruptions which man has witnessed, including those important outbreaks which have occurred since the first edition of the work was published. The numerous high-grade illustrations add much to the volume. The titles of the six chapters indicate the range of the contents and are as follows: The life history of volcanoes; the products of volcanoes; the dissection of volcanoes; the geological history of British volcanoes; the distribution of volcanoes; the theories of volcanoes. J. B.

10. *Essai sur la genèse et l'évolution des roches;* par Alfred Vialay, ingénieur. 8°, pp. x, 226. Paris, 1912 (H. Dunod et E. Pinat).—This work by a French engineer furnishes an interesting instance of reversion in geological theory, quite as remarkable as some in the organic world. The author has been impressed by the great variety and range in chemical composition exhibited by igneous rocks and has attempted an explanation of this diversity which is quite unlike magmatic differentiation, assimilation, or other current hypotheses. He has approached the problem from the standpoint of the chemist, with little or no regard for the facts of occurrence or the inner characters of the rocks themselves, as established by microscopical research.

M. Vialay revives the Wernerian hypothesis that most igneous and metamorphic rocks are in fact of aqueous origin. They are conceived as derived by metasomatic processes from basalt or diabase; these being regarded as in fact nothing but altered greensand and allied marine deposits included under the French term glauconie. The potent agency invoked to accomplish this metasomatic change or diagenesis is carbonated water at a temperature not exceeding 150° or 200° C. Voluminous citations from Bischof, Mohr, Sterry Hunt, Roth and others are given to show the character and great extent of the changes effected by circulating waters. Rocks more siliceous and alkalic than diabase and basalt are products of the leaching action of carbonated water, which removes magnesia, lime, iron and soda more readily than alumina and potash. Thus diabase passes into diorite, syenite and granite, while basalt yields andesite, dacite, phonolite, trachyte and liparite. More complex processes have produced other extreme variants from the sedimentary rock.

Dikes are considered as simply the filling of fissures by deposition from solution. Basalt is not a volcanic rock, in the view of M. Vialay, at least not in the great basalt fields of the world. The proof of this lies in the frequently observed interstratification of basalt and sediments. The presence of rounded quartz grains in basaltic rocks is cited as confirmatory evidence of their sedimentary origin. The reports of Becker on the quicksilver deposits of California and Leith on the iron-bearing rocks of the Mesabi range are regarded as furnishing most valuable support for the author's view. Volcanoes are regarded as having furnished but a small part of the rocks commonly referred to as volcanic. And volcanoes are but superficial, local phenomena whose lavas represent original sediments fused by relief of pressure at certain points. The views of Milne and the Japanese seismologists as to the relation of volcanic and earthquake phenomena are cited as demonstrating that volcanoes have no deep-seated significance. W. C.

11. *Atlas der Krystallformen;* von VICTOR GOLDSCHMIDT. Prospectus, 8 pages and 8 plates. Heidelberg, 1913 (Carl Winter's Universitätsbuchhandlung).—Many years have passed since the publication of the classic Atlas of Crystal Forms by Professor Schrauf. Only one volume was completed; this was begun in 1865 and finished in 1877 and included the species from A to C. A similar work has now been undertaken by Professor Victor Goldschmidt of Heidelberg, and all workers in mineralogy will be gratified to learn that it is rapidly approaching completion. The prospectus now issued states that the work will embrace from 25,000 to 28,000 figures; these will be included in five or six volumes of about 250 plates each, with a like number of volumes of text. Several sample plates are furnished with the accompanying text, which gives a statement of the literature, the list of forms, etc. There are, for example, 21 figures of amalgam and nearly 100 of amphibole, with more of hornblende to follow. It is obvious that the work will leave nothing to be desired in the way of fullness and accuracy, and it should be in the hands of all working mineralogists and crystallographers. Orders for the first volume are now called for, including the species from Adamine to Buntkupfererz (bornite); each volume of the text costs 12 marks and the atlas 20 marks, with an additional charge of 5 marks for a permanent binding.

III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *The Carnegie Foundation for the Advancement of Teaching. Seventh Annual Report of the President,* H. S. PRITCHETT, *and of the Treasurer,* R. A. FRANKS. Pp. vi, 194. New York City, October, 1912 (576 Fifth Avenue).—The total endowment of the Carnegie foundation at the close of its year, on September 30, 1912, was something more than $14,000,000, and the income amounted to about $676,500, all of which, with the exception of some $42,000, was expended. Since its inception the Foundation has distributed a grand total of $2,316,400. At the end of the past year there were 315 professors receiving retiring allowances,

and 83 widows receiving pensions. The list of accepted institutions was not increased during the year; it now includes 72 universities, colleges, and schools of technology. After the introductory statement of the business of the year, Dr. Pritchett proceeds to discuss the general subject of pension systems, particularly as applied to teachers in schools and colleges. This is a subject which, in its widest application, is very much before the public at the present time, and the information concisely given here as to the various systems, political, industrial, and educational, will be of great value to all studying the problem. The suggestions as to a feasible pension system for teachers in the public schools particularly deserve consideration, since they are based on careful study and the six years of practical experience of the Foundation.

Part II, as usual in these reports, is devoted to the discussion of certain problems concerning education; these include entrance acquirements, admission to advanced standing, advertising, and other important matters. It is remarked with satisfaction that in respect to medical education, as to which the Foundation has taken a vigorous stand, much progress toward a higher standard has been made during the last five years. This is particularly shown in the high rate of mortality among medical schools of low grade, the total number of medical schools in the United States having been reduced by about one-third and the students by one-fourth. The problem of State appropriations to institutions under private control is a comparatively new one, and is shown to need careful consideration. It will doubtless surprise many to learn that there are still in this country a considerable number of sham institutions giving collegiate degrees. The frank ventilation of the subject should do much to encourage legislation to prevent this evil.

2. *The Crocker Land Expedition.*—The expedition to explore Crocker Land in the Arctic, planned for 1912 but postponed because of the death of George Borup (see vol. xxxiv, p. 97), has been financially reorganized and a scientific staff secured which promises the most satisfactory results. The leader and ethnologist is Donald B. MacMillan; Ensign Fitzhugh Green, U. S. N., will have charge of map work, terrestrial magnetism, etc.; W. E. Ekblaw, of the University of Illinois, is the geologist and botanist; M. C. Tanquary of the State Agricultural College, Manhattan, Kansas, the zoologist; a well-equipped surgeon has also been selected. The U. S. Navy Department in addition to detailing Fitzhugh Green has added an expert electrician to manage the wireless outfit, provided by the General Electric Co., which will be sufficient for the transmission of messages 2,000 miles, enabling the Expedition to keep in touch with the outside world during its long stay in the North. The addition of the zoologist is made possible by a subscription from the University of Illinois.

3. *Transcontinental Excursion of 1912.*—The March number of the Annales de Géographie, the leading French journal of

scientific geography, gives all its 100 pages to eight essays on selected topics especially studied by the eight French members of the Transcontinental Excursion by which the American Geographical Society of New York celebrated its sixtieth birthday last summer. Bastian describes the canals of New York; Demangeon, Duluth and the Minnesota iron district; de Martonne, the Yellowstone National Park; Baulig, the lava plateaus and the Grand Coulee of Washington; Herbette, the Ports of the Northwest; de Margerie, Crater Lake and Meteor Crater; and Gallois, Utah; and Vacher, Phoenix, Ariz., and the Roosevelt dam. The illustrations are well chosen and exceptionally well reproduced. W. M. D.

4. *The Plant Alkaloids;* by THOMAS ANDERSON HENRY. Pp. viii, 466. Philadelphia, 1913 (P. Blakiston's Son and Co.).—With the development of organic chemistry groups of chemical compounds once regarded as well-differentiated have been shown to possess relationships hitherto unsuspected. The word alkaloid was originally used to describe all organic bases, including the natural alkali-like substances which occur in plants. This definition can no longer be maintained in its original interpretation. Compounds of closely related character not found in nature have been synthesized in the laboratory and put side by side with the vegetable products. Basic nitrogenous substances of all degrees of complexity are now known; and obviously these cannot be grouped under a common head. The physiological action, once a feature strongly emphasized, can now scarcely be used as a distinguishing character. It will be seen, accordingly, that a rigid definition of an alkaloid cannot be formulated. The author uses the term to refer to "a relatively complex basic substance, occurring naturally, and possessing some physiological action." Under this definition the compounds are reviewed in chapters on: the pyrrole group, the pyridine group, diheterocyclic nuclei, the quinoline group, the isoquinoline group, the glyoxaline group, the purine group, and other less well-defined groups. The treatment is both historical and descriptive; and one learns that the literature on the subject has become little short of bewildering without the aid of a guide like this reference work which has few competitors at present. L. B. M.

5. *Household Bacteriology for students in domestic science;* by ESTELLE D. BUCHANAN and ROBERT E. BUCHANAN. Pp. xvi+536. New York, 1913 (The Macmillan Co.).—Until very recently bacteriology has been presented almost solely as a science having its chief applications in medicine and surgery. This attitude is now rapidly changing; and the relations of bacteriology to other problems of everyday life are better appreciated. The present volume is one of the pioneer attempts to emphasize the place of bacteriology in the study of domestic science. Morphology and classification, methods of cultivation of microörganisms, etc. form the introduction, as it were, to a consideration of their rôle in fermentations of various sorts, as well as their rela-

tion to health and disease. Yeasts, molds and pathogenic protozoa are included with the bacteria proper. The book is an interesting illustration of the shifting viewpoint in the academic treatment of the science of bacteriology. L. B. M.

6. *Das Lebensmittelgewerbe—Ein Handbuch für Nahrungsmittelchemiker, etc.;* unter Mitwirkung herausgegeben von Professor Dr. K. von Buchka. Band I, Lieferung 1. Leipzig, 1913 (Akademische Verlagsgesellschaft m. b. H.).—The title page of this new manual relating to the domain of the food industries and food chemistry is indicative of the audience which it intends to reach. A work of two volumes is projected, with the collaboration of ten food chemists and directors of inspection laboratories. The plan outlined includes a consideration of the foodstuffs as they occur in natural products; of alcoholic beverages, spices and other food accessories; and of the adulterations commonly practiced in connection therewith. Apparently it is intended to emphasize the technology of the food trades.

In view of the numbers of books dealing with similar topics which have come into prominence as the result of public agitation on foods, one naturally looks for features of novelty in any fresh essay in the field. The first "Lieferung," containing chapters on Human Food and Generalia as an introduction to the series, fails to reveal any unusual view-points. The discussion of human nutrition does not depart from the conventional statements found in German text-books of physiology; and the chemical portions exhibit a lack of an up-to-date character such as we find in American or English texts on biochemistry. Perhaps this is due to the brevity of treatment adopted. The forthcoming more technical parts will doubtless permit a more critical estimate of the usefulness of the new venture. L. B. M.

7. *A Manual of Immunity, for Students and Practitioners;* by Elizabeth T. Fraser, M.D. Pp. 199. Glasgow (James Maclehouse and Sons), 1912.—The new science of immunity, which has made such rapid strides in recent years, has acquired an aspect of complexity and a nomenclature of its own, both of which tend to detract from the interest that the busy practitioner of medicine or the casual student of biological science may be expected to exhibit therefor. This volume aims to put the reader in touch with the progress which has been made and to give him some appreciation of what the newer features of immunity in its biological, therapeutic, and diagnostic applications are. The subject is presented in a style that will interest rather than repel those who ought to become familiar with these novelties of science. It is sufficiently detailed to enable physicians to get a helpful conception of the present-day status of sero-diagnosis, vaccine and serum therapy. The historical relations of the topics are introduced in a fitting way. That the volume is not devoid of critique is shown by the author's discussion of Ehrlich's "side-chain" theory; of which she says, quoting Huxley, that "Science commits suicide the moment it adopts a creed." L. B. M.

8. *Who's Who in Science. International, 1913.* Edited by H. H. STEPHENSON. Pp. xvi, 572. London (J. & A. Churchill).—The new edition of the "International Who's Who in Science" has increased very largely in size, the 323 pages for 1912 having become 572 for 1913. This alone shows the enterprise of the management, and indicates how much the value of this work has increased. Not only have the existing sections of science been expanded, but the subjects of psychology and geography have been added also. Furthermore, in addition to the valuable series of the world's universities, occupying thirty-four pages, there is a section of nearly twice the extent giving the world's societies. Both these sections are independent of the biographical list (pp. 93–533) including about 7500 notices and the index classified by subjects and countries (pp. 534–569). It is obvious, therefore, that this volume contains a large amount of just such information as those concerned with science and scientific men need. It might be noted that the English language is used throughout, except in the names of journals and of societies. The frontispiece gives portraits of five prominent scientists who died during 1912.

9. *Descriptive Astronomy;* by FOREST R. MOULTON. Pp. 259; 111 figures. Chicago, 1912 (American School of Correspondence).—Professor Moulton is widely known as an original and resourceful investigator of great ability in the field of mathematical astronomy. The volume under review exhibits a philosophical turn of mind and a constructive imagination of equally high order with his power of mathematical analysis. Any person possessing a fair degree of acquaintance with the general field of astronomy will read it with keen interest, but a beginner would fail to appreciate much of its valuable information. It does not appear from the title or preface whether it is designed for a text-book or not, but if so designed it will not, in the reviewer's opinion, prove successful.

The style is easy and the illustrative diagrams admirable, but the early chapters are too rich for class-room food. For example, in the first chapter there is given a most interesting treatise on the earth's atmosphere. It contains an exposition of the method of calculating the height of a meteor, an account of the electrical theory of the aurora and of the kinetic theory of gases, and a discussion of atmospheric conditions on the moon and on the planet Jupiter. Immediately following this the annual motion of the earth is demonstrated by stellar parallax, by aberration and by the shifting of lines of stellar spectra. Each topic is admirably presented, but in this first chapter the beginner is carried like a Cook's tourist through the realms of science. This method does not detract from the excellence of the book, than which of its kind there is none better. Cook's tours are exceedingly useful, though not for the education of children. There are text-books in profusion for purposes of class-room work and a few of them are as good as need be. Probably the author, realizing this, did not set out to write a text-book but an up to date book of reference. W. B.

10. *Algebra for Beginners;* by C. GODFREY and A. W. SIDDONS. Pp. xi, 272. New York, 1912 (G. P. Putnam's Sons) Cambridge (University Press).—The work of experienced teachers who have devised very ingenious and useful methods for presenting the elementary processes of algebra in a way to bring conviction to the mind of a child without any attempt at formal reasoning. Especially happy are the inductive processes of explaining the nature and method of formation of an algebraic equation and of developing the subject of the graph. The exercises are fresh and numerous and full of local color. W. B.

11. *Tables and other Data for Engineers and Business Men;* compiled by CHARLES E. FERRIS. Pp. 169. Published by University Press, Knoxville, Tenn. 1912.—The object of this manual, as stated in the preface, is "to secure a medium whereby we may bring before the minds of the men who control the affairs of the South the strongest possible arguments in favor of technical education as a means of developing our undeveloped resources." There must be other means of effecting this important purpose which would appeal more powerfully than a set of tables to the leaders of industry, but this involves no expense. W. B.

12. *Snyder and Hutchinson's Elementary Text-book on the Calculus;* by VIRGIL SNYDER and JOHN IRWIN HUTCHINSON. 12mo, pp. 384. New York, 1912 (American Book Co.).—Intended to present the calculus in as simple and direct a form as is possible consistently with accuracy and thoroughness. While intended primarily for students in engineering and science, it meets the requirements of all beginners in the calculus equally well. There is a refreshing absence of the superfluities often noticed in elementary text-books which strive for a degree of rigor which the student cannot appreciate until practice has made him acquainted with the subject. W. B.

13. *The Science Reports of the Tôhoku Imperial University, Sendai, Japan.*—The Tôhoku University established in 1912 a series of Science Reports, of which several numbers have already been issued. The librarian of the University, Professor T. Hayashi, is chairman of the publication committee. Two Series have been inaugurated; one of the numbers now in hand of the First Series contains an interesting paper by Mr. Katayama on the nature of atomic weight; another by Mr. Kobayashi on the composition of the remarkable uranium mineral called thorianite. The author finds two varieties, one containing 78 per cent of thorium oxide and 15 per cent of uranium oxide, the molecular ratio of ThO_2 to UO_2 being closely 6 : 1. The second kind contains 60 per cent and 33 per cent respectively, with the ratio of 2 : 1. The first number of the Second Series (in quarto form) is devoted to geology and gives a paper on the lime algæ of Japan and China by H. Yabe.

14. *Bibliotheca Zoologica II. Verzeichniss der Schriften über Zoologie welche in den periodischen Werken enthalten und vom*

Jahre 1861–1880 selbständig erschienen sind; bearbeitet von Dr. O. Taschenberg. Neunzehnte Lieferung. Leipzig, 1913 (Wilhelm Engelmann).—This nineteenth part of the comprehensive work edited by Dr. Taschenberg (earlier noticed in this Journal) includes signatures 721–744 and pages 5801–5992. It completes the first half of volume seven of the entire work and is largely devoted to the titles of works dealing with natural history travels in different lands.

15. *Atlas de la República de Chile.*—A valuable map of Chile with the above title on its cover, but named "Mapa escolar de Chile" on one of its pages, has been constructed under the direction of Chief Engineer Jose G. del Fuenzalida and published on the scale of 1:1,500,000 in a series of nine sheets in ten or more tints (six shades for land altitudes, and five for sea depths) by Justus Perthes of Gotha in 1911. A series of twelve cross profiles on a horizontal scale of 1:1,000,000, with tenfold vertical exaggeration, give effective presentation of the relief. The contrasts between the desert basins of the north, the populous agricultural valleys of the middle section, and the glaciers, lakes and fiords of the far south are well brought forth. W. M. D.

16. *The Prehistoric Period in South Africa;* by J. P. Johnson. Second Edition, Revised and Enlarged, with a Map. 115 pages. London and New York, 1912 (Longmans, Green and Co.).—In his preface the author frankly acknowledges that the new edition contains very little new material except the chapter on Coast Middens, made possible by Dr. Peringuey's publication of specimens in the Capetown Museum; and Appendix I: The Sequence of Stone Implements in the Lower Thames Valley, by A. S. Kennard. For a review of the first edition, the reader is referred to this Journal, xxxi, 578, 1911.

Middens occur from Walfisch Bay on the west to Delagoa on the east. Small stone flakes like those from the inland sites are found in the middens; finished implements are rare. The debris from the caves along the coast is similar to that from the middens. Burials in the middens and caves are of the same type: Doubled in such a manner as to bring the hands and knees near the chin. Ostrich eggshell beads are the usual accompaniment and flat stones lie directly on the skeletons. In the Coldstream Cave three stones were found on which drawings were executed in black. On one of these the four drawings represent human beings with prominent calves and buttocks. As for the sequence of stone implements in the lower Thames valley, Mr. Kennard believes in the human origin of some of the eoliths from the Kent Plateau. The later horizons include: Proto-Chellean, Chellean, Acheulian, Mousterian, (?) Magdalenian, neolithic, bronze, and iron.

G. G. MACCURDY.

17. *The Origin and Nature of Life;* by Benjamin Moore. Pp. 256, 12mo. New York (Henry Holt and Company) and London (Williams and Norgate). Home University Library of Modern Knowledge, No. 63.—The magnitude of the subject and

the size of this volume are hardly in accordance, but there is much to interest the general reader and he may well be prompted to extend his studies further. In the first eight chapters, in the words of the author, "a continuous process of evolution has been traced from the electron to the atom, from the atom to the molecule, from the molecule to the colloid and so on to the confines of the organic world." The concluding chapters discuss "the living organism at work" and "the cyclic activities of life."

OBITUARY.

Oscar Dana Allen, Professor of Analytical Chemistry and Metallurgy in the Sheffield Scientific School from 1871 to 1887, died at his home in Ashford, Washington, February 19th, 1913, at the age of 77 years. He was born at Hebron, Maine, was graduated from the Sheffield Scientific School in 1861, and received the degree of Ph.D. from Yale in 1871. When obliged to retire from his professional work on account of ill health, he took up his residence near the foot of Mt. Ranier. His wife and three sons survive him.

Professor Allen was distinguished for his profound and wide learning, as a chemist, a mineralogist, a botanist, and a linguist. Early in his scientific career he extracted a large quantity of cæsium from the lepidolite of his native region, and in collaboration with the late Professor Samuel W. Johnson, he greatly advanced the knowledge of this recently discovered element, and made the first accurate determination of its atomic weight. He edited an American edition of Fresenius's Quantitative Analysis, and modernized its nomenclature.

In mineralogy he took much interest; he made a notable mineral collection, and investigated the composition of a number of minerals, being particularly interested in those of rare or complex character.

He was an admirable teacher, arousing much enthusiasm in his students, and thus was instrumental in the development of a number of prominent chemists and metallurgists. He was also an enthusiastic botanist, and carried his studies in this line to some of the lower orders of plants. After his retirement he was fortunate in being able to carry on important botanical work in a new region. Further, he took great interest in languages, and was accustomed to make the acquaintance of foreigners in order to get instruction in their tongues, some of which were obscure; in German he gained much proficiency during a period of study at the Bergakademie in Freiberg. His memory of words was remarkable, and he was fond of tracing their roots through various languages.

Professor Allen was much admired by his many friends for his genial and kindly personal traits. He was inclined to be retiring and unconventional. He once said that he liked the motto "*Esse quam videri*," and it seems that he lived according to that idea.

H. L. WELLS.

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SCIENTIFIC INTELLIGENCE.

VOL. XXXV. JUNE, 1913.

Established by **BENJAMIN SILLIMAN** in 1818.

THE
AMERICAN
JOURNAL OF SCIENCE.

EDITOR: EDWARD S. DANA.

FOURTH SERIES

VOL. XXXV—[WHOLE NUMBER, CLXXXV].

No. 210—JUNE, 1913.

NEW HAVEN, CONNECTICUT.
1913.

THE TUTTLE, MOREHOUSE & TAYLOR CO., PRINTERS, 123 TEMPLE STREET.

Published monthly. Six dollars per year, in advance. $6.40 to countries in the Postal Union; $6.25 to Canada. Remittances should be made either by money orders, registered letters, or bank checks (preferably on New York banks).

THE

AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

Art. XLVII.—*Relationship between Terrestrial Gravity and Observed Earth-Movements of Eastern America;* by J. W. Spencer.*

Contents.

Introduction.

This paper has been suggested by the remarkable charts of Mr. William Bowie, delineating the results of gravity investigations,† for at once I recognized in their anomalies a relationship to the later earth-movements, which have long been special subjects of my own studies. These determinations of terrestrial gravity throw a wonderful amount of additional light on at least three problems:—1, The changes of level of land and sea, as proved by the occurrence of the submarine cañons and valleys indenting the border of the Continent; 2, the post-glacial deformation measured on the deserted beaches of the Great Lakes and the cause of the rocky barrier which partly obstructs the Ontario basin; and 3, the fallacy of attributing the post-Glacial deformation of the lake regions to melting of the glaciers. This mere statement shows the great value of knowing the intensity of gravity in studying the final

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* Read before Phil. Soc. Wash., D. C., May 10, 1912.

† "Effects of Topography and Isostatic Compensation upon the Intensity of Gravity," by Wm. Bowie; Special Pub. No. 12 (2d paper), U. S. C. & G. Survey, 1912.

evolution of our physiography whether geographical or geological.

With additional data obtained at intermediate points, the contours of anomalies of gravity will be somewhat modified. The points for new determinations which promise the greatest results would seem to be along the lines of greatest tilting measured in the raised beaches, and others crossing the mountains and extending to the coast; also along other lines prolonged northward to beyond the Canadian highlands.

Submarine Valleys and Cañons Indenting the Border of the Continent.

Having made extensive studies of these features,* and also published a recent summary of them in Hull's "Suboceanic Physiography of the North Atlantic," which is a monograph in atlas form,† only a general reference need here be made to them. The submarine cañon of the Hudson is the one most completely surveyed. It has a length of fifty miles and has been found to reach a depth of over 7,000 feet below sea level. The winding trench itself has a depth in one locality of 4,000 feet. It is also characterized by a succession of steps.

The St. Lawrence River has a depth of over 1000 feet where the estuary widens out into the Gulf, through which extends a broad valley (to a depth of 2000 feet, with high banks) reaching to the border of the Continental Shelf, which is here incised by a cañon to an undetermined depth, similar to that of the Hudson. Like features occur off the Gulf of Maine, beyond Chesapeake Bay, between Florida and the Bahamas, and in extensions of the Mississippi and probably of all other rivers entering both the Atlantic and the Gulf of Mexico.

The submarine continental slope is also characterized by platforms or terraces, notably between 2400 and 3000 feet.

All of these valleys are pure topographic forms of erosion in plateau regions. They are not of exceptional occurrence, but have already been noticed in scores if not hundreds of instances. There is no other geological or geographical explanation of their origin, supported by any evidence, than that they were formed by stream erosion at a time when the land was at a higher level, or the sea lower than now.

Such changes of level in modern geological times seem staggering to those who ignore these great features, or, as I have heard it said, that such an explanation is discredited by the studies of Prof. John F. Hayford, relating to isostasy, in showing that the continent is now nearly balanced in its relation to ocean areas. But Hayford says: "There is abundant geologi-

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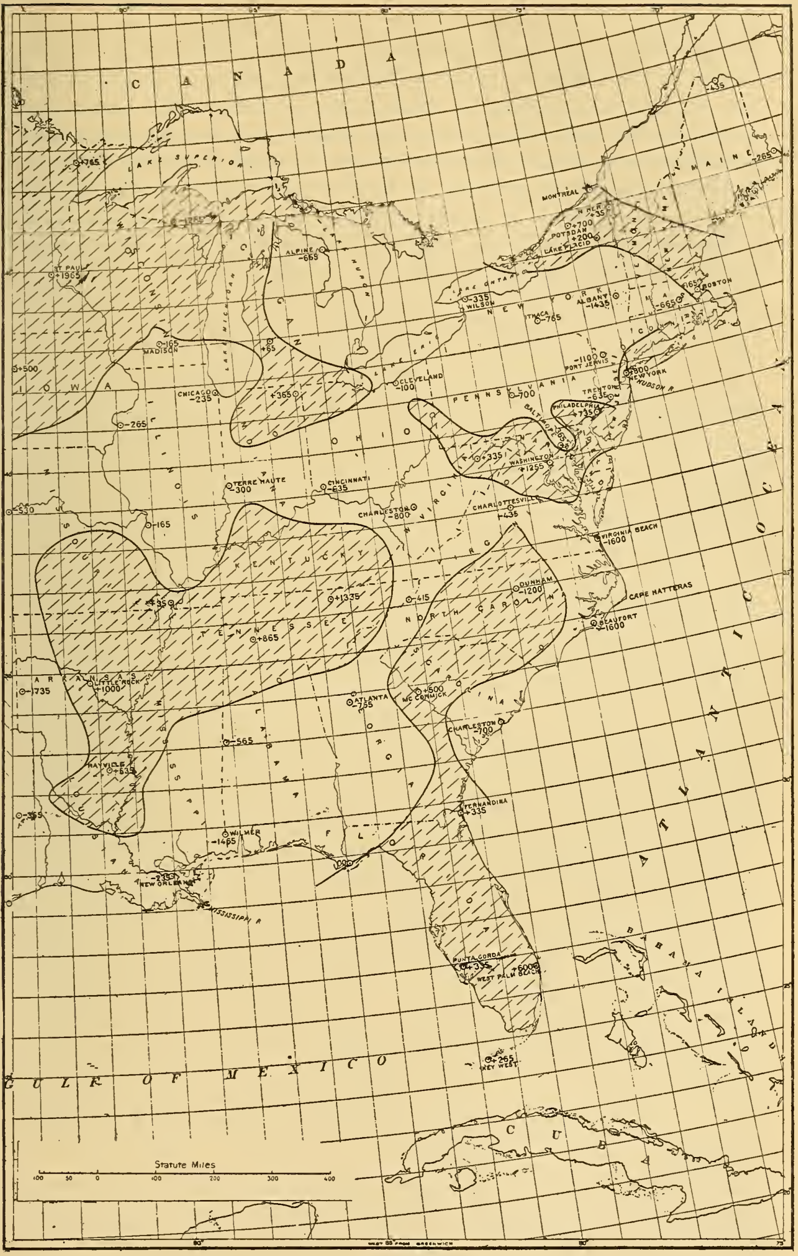
* These have appeared in the Bull. Geol. Soc. Am., this Journal, etc.

† Published by Edward Stanford, No. 11 Long Acre, London, W. C., 1912.



ANOMALIES OF TERRESTRIAL GRAVITY (after Bowie).

Shaded area represents excess (+) and unshaded deficiency (−) in intensity—both calculated in terms of thickness of rock-strata in feet, as given in figures on map.

ERRATA on map: At New Orleans read −430; at Beaufort −700°; at Durham + in place of −.

cal evidence that within the interval covered by the geologic record, many thousands of feet of material have been eroded . . . and deposited in other parts, that changes of elevation of the surface, amounting to thousands of feet, have been produced in this and other ways, and that these changes have continued to take place in recent times."* Let us examine some of the anomalies of gravity in their relationship to the theory of changes of land in late geological days, of which we have found so much evidence in the submarine valleys indenting the border of the continental mass.

Relationship of the observed Earth-movements and Intensity of Gravity in Eastern America.

Preliminary studies of the recent terrestrial deformation in the Appalachian belt indicate that there is an increasing rise from zero at Washington to three feet per mile, or possibly five feet or more, in proceeding up the Potomac valley. Southeast of the city there is depression to the mouth of the Chesapeake Bay, where the original valley is deeply buried by the sands of the bottom of the bay. On following up the Susquehanna valley, I have not so far found a greater deformation indicated than three feet per mile. In Georgia there is the same evidence of tilting in recent times, with a rise towards the mountain zone and a sinking towards the sea. The intensity of gravity at Washington, according to Bowie,† shows an excess of weight equivalent to about 1255 feet of rock, while at Virginia Beach, 150 miles distant on the coast, a deficiency of weight occurs equal to 1600 feet of rock Thus, if the whole region had been equally heavy, the difference of weight would represent a subsidence of 2855 feet.

The physiography of the region presents unusual features, in that the coast at Cape Hatteras is situated only a few miles from the border of the continental shelf, an entirely different condition from that of any other point along the coast. Also, beneath the sea, a very large and deep embayment in the continental slope occurs in front of Chesapeake Bay (with the valley of which it was doubtless connected), similar to the features about the cañon of the Hudson. It has appeared to me that the coastal plain of the region about Cape Hatteras has been built out upon the continental shelf by the materials brought from the mountain zone behind, and in support of this

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* Science, vol. xxxiii, p. 3, 1911.

† In this paper only the New Method (Hayford) anomalies of gravity are considered. They are shown on Chart No. 2, Spec. Pub. No. 12, Coast and Geodetic Survey. According to Bowie, ·003 dyne (unit of force) increase in gravity may be assumed, as a working hypothesis, to be caused by a disk of rock of average density (of 2·67), of indefinite horizontal extent and 100 feet in thickness. Ib., p. 22.

view there is a deficiency of weight, extending inland, which amounts to 435 feet at Charlottesville, Va. The reduced gravity in proceeding from Washington to Baltimore (where it is minus 365 feet of rock) might be expected, owing to the long denudation of the Susquehanna-Chesapeake valley.

In the Great Lakes region I find that the greatest amount of recent deformation is observed in passing from the zones of the less rigid rocks to others more so.

Other examples of great variation of gravity, amounting to 1900 feet of rock, appear between Durham and Beaufort, N. C., and 1200 feet between McCormack and Charleston, S. C., but this latter reduced difference might be expected, as Charleston is situated much farther from the border of the continental shelf than the other points mentioned.

The anomalous intensity of gravity in Florida, especially in the southeast part of the state, is of very great interest. It is overweighted to even 600 feet, like the mountain zone to the northward, in place of being underloaded as on the coastal plain of the Carolinas. The Bahamas are, manifestly, the remains of a great dissected coastal plain in front of Cuba, and now the gravity determinations indicate that the islands and coastal plains were situated in front of Florida, which was a backbone (although now plains), in place of their extension westward over the peninsula. Thus this anomaly further demonstrates the former continental connection of the West Indian island masses.

The intensity of gravity along the Gulf of Mexico shows underloading, as is the case along the Atlantic border. But it is surprising that at New Orleans there is a deficiency of 430 feet, in spite of the enormous load of mud being constantly carried into the Gulf. Borings at New Orleans show that the bottom of the old valley is not reached at 1000 feet. Prof. G. D. Harris has found that several deep valleys have been cut through the old Tertiary strata in Louisiana, to the west. These have since been refilled with deposits containing only living species of shells to depths of 2,300 feet, thus showing a recent subsidence to this amount, which he thinks should reach 3,000 feet at the Mississippi. It may be suggested that the refilling of the valley does partly account for the reduction of a greater deficiency of gravity, as seen at Wilmer, a hundred miles to the northeast, where it is 1,465 feet too light.

The excess of pressure at Philadelphia is equal to 735 feet of rock, but this zone is replaced at Princeton by one of deficiency (635 feet). At New York overloading occurs to 800 feet, but the district on land of excessive weight is small, as if the zone extended out on the continental shelf. It reappears at Boston, while Maine seems to be underweighted, but this region must be connected with that of the St. Lawrence river.

Two other areas of anomalies may here be mentioned as being of relative importance in a later part of this paper. At Olympia, Washington, a small district is overloaded by 1,100 feet, while fifty miles away, at Seattle, the deficiency of gravity equals 3,100 feet of rock, or a total difference of 4,200 feet. The narrow coastal plain along the Pacific coast is deeply incised with cañons as on the east coast. St. Paul is in an area of more than 400 miles in diameter, where the overloading increases to 1,965 feet, but this is in the interior of the continent, yet outside this area underloading occurs over great areas.

Relationship of Terrestrial Gravity to the Deformed Beaches and Rock-barrier of Lake Ontario.

The abandoned shorelines about the Great Lakes are found to have been raised from zero to six feet per mile in proceeding towards the northeast and north. The investigation of terrestrial gravity throws the first direct evidence as to the cause of the deformation.

The most important of the old shore-lines for determining the recent earth-movements are: (1) the Iroquois Beach (of the Ontario Basin),* (2) the Forest Beach of the former Lake Warren (when the waters of the Huron, Erie and Ontario basins were united at the same level), and (3) the Algonquin Beach of Lake Algonquin (Lakes Huron, Michigan, and Superior united into one body of water), with its outlet eastward, in place of by the Detroit and Niagara Rivers.†

The present deformation of the Forest Beach, between Cleveland and Font Hill (12 miles west of Niagara Falls) is 120 feet. This may be correlated with that of the Iroquois Beach, at the head of Lake Ontario. Here it is 363 feet above sea-level, but rises to 637 feet, at a point 130 miles distant, on the northern side of the lake,‡ near which it becomes lost, as if obstructed by a glacial dam. Following the beach around the southern and eastern margins of the lake, I found that its height rose to 730 feet, near Watertown. This deformation of 367 feet was instrumentally measured. Beyond, the old shore-line was most difficult to follow, owing to the more rugged character of the country, but as located at Parishville,§ nine

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* This beach was first described by the writer in a paper read before the Phil. Soc. Washington, Abstract in Science (1888) and published in full in Trans. Royal Soc. Canada, vol. vii, Sec. iv, pp. 121–132, 1889. This Journal, vol. xl, 1890.

† The discovery of Lakes Warren and Algonquin, by the writer, was announced at the Cleveland meeting, Am. Assoc. Adv. Sc., 1888, with abstract in the Proceedings, vol. xxxvii, pp. 187–199, 1889; this Journal, vol. xli, pp. 12-21, 202-211, 1891. See "Falls of Niagara," by J. W. Spencer, Geol. Surv. Can., 1907.

‡ This Journal, vol. xl, pp. 443–451, 1890.

§ By Fairchild, and subsequently by the writer.

miles southeast of Potsdam, it is about 903 feet above sea-level. Consequently the post-glacial tilting is 540 feet, occurring mostly about the eastern end of the lake and beyond. This deformation has raised a rocky barrier across the St. Lawrence valley under a drift covering, which is deep in the buried channel. The obstruction to the Ontario basin extends to Montreal, where the last rapids are located. There is no further impediment to the river below this point. In the vicinity of the uppermost rapid the maximum warping is computed to be 750 feet. If the tilting be carried back to Cleveland the measured rise thence to the vicinity of Potsdam is found to reach 660 feet. The pendulum measurements have been made at these points.

From the map of this new chapter in geodesy by Mr. Wm. Bowie, the excess of weight at Potsdam* represents an overloading of 700 feet of rock (corrections for elevation above the sea having been made in gravity reduction). The probable error of each station is about 100 feet. At Cleveland the underloading is equal to 100 feet of rock. These total 800 feet. Is the closeness of these figures a coincidence or a confirmation of both methods? Perhaps both.

East of the mouth of the Niagara River (at Wilson) a deficiency of gravity occurs equal to 335 feet of rock. This increases the differences in the two measurements of the St. Lawrence bulge, part of which may be in the figures, or be due to earlier deformation not recorded in the beaches, or perhaps to the denudation in the Ontario valley, before or during the earlier Glacial period. The underloading is also shown at Ithaca, situated on the highlands, where it is equal to 765 feet of rocks removed.

The underweighting in the Finger Lake region suggests a greater deformation than is found in the beaches of later date, thus further explaining the great depth of their pre-glacial channels, and discrediting the hypothesis of their glacial origin.

All of the anomalies of gravity limit the overloading to the Saint Lawrence bulge of northern New York, while the remainder of the state (except New York City), Pennsylvania to near its southern boundary, and most of Ohio, are underloaded. On the eastern side of the bulge the excess of gravity is reduced to 30 feet of rock at North Hero, on the peninsula at the northern end of Lake Champlain, and beyond, to the northern point of Maine, this region south of the Saint Lawrence is supposed to be underloaded. This corresponds with the absence of rocky barriers across the river below Montreal.

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* The excess observed here seems to be independent of the density of the rocks, for at Lake Placid, among crystalline rocks, to the south, it is only +200 feet. The deficiency of 1,600 feet at Virginia Beach is not due to the lighter Cretaceous and Tertiary strata, which are probably about 2,200 feet thick over crystallines, as this is their thickness at Norfolk, a few miles away.

Thus, I find a remarkable agreement between the results of my own physiographic researches and the geophysical investigations of Hayford and Bowie, so that no other explanation of the deformation of our great drainage seems possible, than that the tilting is due, either to an excess of matter, squeezed in at a considerable depth (thus raising the land as appears in the deformed shore-lines), or to a differential sinking of a great elevated area increasing in rate, on receding from the zone of more rigid rocks, which last hypothesis I have been approaching for some time, and here propose. The surface effects would be the same in both cases. This problem will require another chapter.

As no gravity determinations have been made in Canada, one must depend alone on the physiographic investigations. By these I have shown that the focus of maximum post-Glacial elevation is located about 300 miles north of the outlet of Lake Ontario (near latitude 49° N., longitude 76° W.) or adjacent to the axis of the most southern lobe of the Laurentian Highlands.* It is most desirable that a line of gravity stations should be extended to this point. I should expect to find an excess to the mountain axis, but this overloading is hardly likely to extend to Hudson Bay.

From Lake Superior and the states to the west, it would almost seem that the excess of gravity should be found throughout the country all the way to the Laurentian belt of northwestern Canada.

Deficiency of Gravity and the Hudson–Champlain Valley.

The northeastern extension of the Delaware Valley, between the mountain ridges, joins that of the Hudson at Kingston, and appears to have once belonged to the same drainage system flowing northward. But the flattening out of the post-Glacial rise (three feet, as found in the terraces by Woodworth) would not completely explain the deep trench (750+ feet) in hard crystalline rocks at the aqueduct tunnel of Storm King, four miles north of Westpoint.

The anomalies of gravity may throw some light on the subject. At Albany the deficiency is equal to the weight of 1,435 feet of rock, as if the region had sunk 1,465 feet below that of North Hero, 160 miles to the north. Woodworth shows a deformation of 650 feet† between these points, or about half of the gravity anomaly, with the depression southward. May not there have been additional deformation of the difference in amount before or during some stage of the Gla-

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* Trans. Royal Soc. Canada, 1888, cited before. Also Jour. Geol., vol. xix, pp. 57–60, 1911. Bull. Geol. Soc. Am., vol. xxiv, 1913.

† Report N. Y. State Museum, Bull. 84, chart opp. p. 226, 1905.

cial epoch? Or is the difference in gravity principally due to transference of materials within the earth's crust? In part, at least, I should be inclined to the hypothesis of an earlier as well as the post-Glacial deformation.

The anomalies of gravity open up a new field for investigating the origin of rock basins in glaciated regions, as the product of erosion during several Glacial, interglacial and earlier periods; where the manner of the supposed ice erosion is unexplained. Not much assistance along these lines can be derived from Europe, until the gravity stations there are reduced by the Hayford method. Finally, Hayford has indicated how a region may sink as well as rise in regions of erosion, thus becoming areas of deposition,* all in conformity with physical laws.

The Fallacy of Post-Glacial Deformation being due to the Melting of Ice caps shown in the Anomalies of Gravity.

The excess of gravity at Potsdam, N. Y., is equal to the weight of about 2,000 feet of ice. Any resilience of the earth's crust due to the melting of the glaciers should not raise the mass above normal gravity, as is here found. Other examples of anomalies may be given in terms of ice.

The excess of matter at Potsdam over that at Albany, 150 miles distant, is equivalent to 6,000 feet of ice. Both places are in the same glaciated area, which is now everywhere in New York state underloaded, except in the northern part and near New York City.

St. Paul is the center of an area of excessive gravity, more than 400 miles in diameter. In the vicinity of that place it is now overweighted by the equivalent of over 5,400 feet of ice. This region was also covered with glaciers in former times. Beyond the limit of the glaciated surfaces, as between Washington and Virginia Beach, 150 miles apart, the difference of gravity is equal to a thickness of 8,200 feet of ice. The former locality is overweighted while the latter is underloaded. Again a deficiency of 4,200 feet in terms of ice is seen in Alabama, far south of glacial action.

The extraordinary example of differential gravity mentioned as occurring between Olympia and Seattle, Wash., is equivalent to no less than a load of 11,000 feet of ice.

Lastly, reference may again be made to the enormous quantity of sediments carried down the Mississippi River, but these have not yet balanced the underloading near its mouth, while in contrast the country about the mouth of the Hudson River, which carries no load, is overweighted.

These illustrations show great terrestrial rigidity, maintained

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* Science, vol. xxxiii, p. 6, 1911.

for a long period, over large areas (less than continental) of both excess and deficiency of gravity, and over those glaciated and not.* The variations of load given are quite equal to the weight of former glaciers, yet without a subsequent readjustment to isostatic conditions, since the disappearance of the ice caps.

Before studying the effects of gravity, I had commenced investigations, in order to ascertain the amount of recent deformation of the mountain zone, south of the glaciated areas, for comparison with that of the lake district. These are now less important, in this connection, since the discovery of the remarkable anomalies of gravity, as found by Hayford and Bowie, in the investigations of the U. S. Coast and Geodetic Survey, under the direction of Superintendent O. H. Tittmann.

These studies confirm the physiographic evidence of deformation, based upon the drainage features both pre-Glacial and post-Glacial.

On the Causes of the Changes of Level.

Hitherto, I have suggested no hypothesis as to the cause of the late continental elevation and subsequent depression, which first enabled the rains, streams and rivers to excavate the deep valleys and cañons along the border of the continental mass, and then submerge the frontal plateaus, slopes and valleys. It has lately been urged on me by one of the most learned investigators of Europe, Sir John Murray, that my task does not end with the description of the phenomena themselves without trying to find their relationship to the final causes. This problem is so stupendous that I should not have dared to announce a working hypothesis had not the anomalies of gravity been found coinciding with my own investigations in the physiographic deformities, since extended and confirmed by Taylor, Leverett, Goldthwait, Fairchild, Coleman.

My hypothesis of the primary causes of the great changes of level on land and sea is that they are due in some way to differential contraction under the ocean and land areas, although very little is known of the physics of the earth. This is not a new idea, and has been expressed in one form or another. For geological purposes it seems to answer best. Under it the

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* The excess and deficiency of materials, even at St. Paul and Seattle, are small compared with the mountain and plateau masses. Bowie states that the gravity determinations indicate that the average excess or deficiency at the stations of observation is about 630 ft., while the average elevation of the United States is about 2,500 feet ; so that the crust is in approximate equilibrium for the country as a whole, at the present time. But the ocean is near its highest level, so far as the coasts are concerned, while formerly it was much lower. (Spencer.)

continents should be raised (perhaps for relatively short periods) with the formation of cañons along their borders, such as actually occur, and subsequently subside to renewed isostatic conditions. Mountain-making movements, block and other faulting, subsidence of deep basins, transportation of eroded materials (with subsequent expansion) and deposition are secondary features. This means also changes of ocean level, in relationship to the continental border, as well as deformation on the land.

I am not aware of the announcement of any explanation of the cause of the deformation of the lake regions other than a hypothetical readjustment after the removal of the ice, which I have here shown to be untenable from the evidence found in the variations of terrestrial gravity, as well as from the physiographic evolution of the lake regions and from the occurrence of similar tilting in the Appalachian belt, south of the glaciated region. My hypothesis is now that this unequal warping of the surface, without thrusts, results from differential sinking of areas, resting on foundations of unequal rigidity, during epochs of subsidence of greater regional, or perhaps continental extent, to which the deformed areas are subordinate, with superficial effects. The explanation of the features of deformation is inseparable from the investigations of the great changes of level found in the submarine valleys.

Summary of Discussion.

The submarine valleys or cañons, dissecting the platforms or terraces on the edge of the continental mass, demonstrate great subsidence of the land, or rise of the ocean level, in very late geological times. Correspondingly, almost everywhere a deficiency of gravity characterizes the continental border, and often extends far inland among the mountains themselves. South of New York, the mountain region is generally overweighted, but bordered on both sides with underweighted zones. Even Florida shows excess of matter, as in the mountain zone. This may be taken as additional evidence of a late union of the West Indies with the continent.

The differential gravity between the Appalachian zone (at Washington) and the coast is equivalent to 2,855 feet of rock strata. Thus the proof of recent changes of level, as observed in the submarine cañons, is supported by investigations of terrestrial gravity, to at least the extent mentioned.

The deficiency of gravity in the lower Mississippi region seems very remarkable, when the river has been carrying down its enormous load for so long a time. In contrast, the mouth of the Hudson River, which transports scarcely any materials, is in a district of overweighting as if the zone extends seaward, while New England appears to be underloaded, as at certain points.

Between Lake Ontario and Lake Champlain, a terrestrial bulge occurs, rising to 660 feet or more, and forming part of the barrier to the Ontario basin (the barrier is partly dissected and overlaid by drift). I have measured this amount of tilting in the abandoned shore lines.

This region is now found to be overloaded to the equivalent of 700 feet of rocks, while the country to the east, south and west is almost everywhere underloaded. Thus the anomalies of gravity confirm the results derived from the survey of the amount of deformation.

At Ithaca and Albany the deficiency of weight is even greater than the excess in the St. Lawrence bulge.

No pendulum measurements have been made in Canada, but there is little doubt that excess would be found extending to the focus of post-Glacial elevation located in the Canadian highlands.

The St. Lawrence bulge is due to terrestrial movements, which have occurred mostly in post-Glacial days, since the birth of Niagara Falls, whether due to squeezing up of materials or to sinking of adjacent regions, which everywhere to the south are now underweighted.

The deficiency of gravity at Ithaca and Albany suggest that the pre-Glacial channels in these regions may owe part of their great depth to slopes, different from the modern ones, deformed in earlier Glacial and inter-Glacial epochs.

The anomalies of gravity show that the St. Lawrence bulge is now overweighted to the equivalent of 2,000 feet of ice, above the normal, or to 6,000 feet above the underloaded region of Albany. At St. Paul the excess of gravity equals 5,400 feet of ice. Both localities are inside the glaciated area. Elsewhere, differential loads have been observed equivalent to even 7,500 and 11,000 feet of ice. The anomalies of gravity, here shown, confirm the fallacy of any hypothesis that the post-Glacial warping described is due to the melting of the ice sheets, which view is also contrary to the physiographic development of the St. Lawrence and Great Lake regions.

A considerable amount of the great changes of level have occurred sometime since the beginning of the Glacial period, which, I believe, may have been extended over a million of years or perhaps much more.

The cause of the great changes of level of land and sea are believed to be due, primarily, to differential contraction of the earth's interior, under the land and ocean areas; that recent deformation of the region of the Great Lakes and Appalachian

Mountains is subordinate to the late continental subsidence, and due to unequal sinking of zones resting on foundations of unequal rigidity.

In the case of the St. Lawrence region, this is in agreement with the post-Glacial changes of level. In other localities this is not so apparent, but suggests earlier movements that we have not so far attempted to determine, which opens a new and wide field. There always remain the possibilities in other localities of the differences being due to masses of unequal density, as in some cases have been shown by Bowie, but these can be correlated in part with the physiographic features.*

This paper must be regarded only as an advanced chapter, as it is the first that has been written on the subject, with only hints as to some of the bearings of the investigation. It may be added that I have seen for three years, that a relationship exists between the late deformation of the lake region and the drowned valley of the St. Lawrence; the results of my researches on the subject are not yet published. Only after studying the new chapter on gravity by Hayford and Bowie, which is epoch-making in the science of physiography, did I find that the earth-movements of the lake region, without lateral thrusts, are subordinate to the greater continental changes of level, and a satisfactory explanation of their origin. This is in fulfillment of the prediction of Prof. J. P. Lesley, twenty-five years ago, made on the first appearance of my paper on "The Iroquois Beach of Lake Ontario," when he wrote: "It is a page in the new history inaugurated in a great measure by yourself, and involving some of the most important points . . . and in fact must throw light on the whole subject of elevation and subsidence as applicable to the entire area of the United States."

Washington, D. C., April, 1913.

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* The anomalies of gravity would be the same whether there has been an increase or diminution of matter at the surface (deposition or erosion) or a transference of some internal terrestrial mass in the earth's crust, adding to or reducing the quantity at various points.

Art. XLVIII.—*A Review of Recent Advances in South African Vertebrate Paleontology*; by R. Broom.

During the years 1911 and 1912 a greater advance has been made in our knowledge of the Karroo vertebrates than in any previous half dozen years. In part this has been due to the visit to South Africa of Dr. D. M. S. Watson: in part to the ability of Mr. S. H. Haughton as a collector and preparator, now on the staff of the South African Museum; but mainly has it been due to the industry of the Rev. I. H. Whaits of Beaufort West, and of the veteran collector Mr. Alf. Brown of Aliwal North.

In almost all of the orders and suborders our knowledge has greatly increased. Watson, Haughton, and Whaits have succeeded in getting so much new Pareiasaurian material that our knowledge of the structure of the group is almost complete. One or two new species have been discovered and a new genus from the Upper Permian which resembles the Russian Pareiasaurs more closely than the typical African forms.

We have now in hand sufficient remains of the Dinocephalia to enable us to publish an almost complete anatomical account of this most interesting group. Though in many ways considerably specialized they are closely related to the American Pelycosaurs, and when the figures of their bones are published it is believed that they will at once be recognized as American types modified to suit other conditions.

In the Dromasauria we now know the hind foot to be almost typically mammalian with a large tibiale and fibulare, a small centrale situated like the mammalian navicular and 4 distal tarsals. A new family is represented by a toothless form.

Though little has been added to our knowledge of the Therocephalian structure a considerable number of new species and genera have been discovered.

Much more important has been the great increase in our knowledge of *Gorgonops* and allied forms. Though in many respects resembling the typical Therocephalian it seems more satisfactory to keep them by themselves in the suborder Gorgonopsia suggested by Seeley. In the structure of the temporal region they agree more closely with the Anomodonts than with the Therocephalians, and in having a single median true vomer they resemble Anomodonts, Cynodonts and mammals. Though the digital formula is 2, 3, 4, 5, 3 there is little doubt that both the Anomodonts and Cynodonts have come from a Gorgonopsian ancestor and that thus this suborder is in the direct Mammalian line.

Though among the Anomodonta less remained to be known we have many interesting new facts. *Oudenodon* is now clearly recognized to be the female of *Dicynodon*. In the skull of *Dicynodon* there is now believed to be a distinct quadrato-jugal, though it is almost always anchylosed to the quadrate and forms part of the articulation. Further, most Anomodonts have a septo-maxillary. In some species it is large; in others it is either rudimentary or absent. In the palate a distinct transpalatine is now recognized. The peculiar bone which was long regarded by the writer as tympanic is now known to be the stapes and this discovery has led to the complete acceptance of the incus-quadrate theory by the writer and possibly others.

Our knowledge of the Cynodonts has been increased by the discovery of a few new forms but chiefly by the detailed investigation of the known skulls by Watson and Broom. The Cynodont skull is now almost as well known as that of the mammal.

Among the Diapsida, using this very handy term for the reptiles other than the mammal-like reptiles, by far the most important find has been the little reptile found by Brown and named by the writer *Euparkeria capensis*. It is a large-headed little animal about 2 feet in length. The skull is sufficiently primitive for it to have been ancestral either to the Dinosaurs, the Pterodactyls or the Birds, or even to the generalized ancestral Phytosaurs such as *Erythrosuchus*. The shoulder girdle has a large coracoid with enclosed foramen. The pelvis is plate-like and might be ancestral to either the Dinosaur or Avian types. The pes has the large Rhynchocephalian 5th metatarsal but in other respects is quite Dinosaurian. There is reason to believe that the animal was at least potentially bipedal. Unfortunately the manus is unknown. Though *Euparkeria* cannot be placed with the Dinosaurs, there is little doubt that it belongs to a group immediately ancestral to the Theropoda—a group to which also belonged the ancestor of the bird and of the Pterodactyls. A curious specialization of the genus is the presence of two pubic foramina. The eye has well ossified sclerotic plates and the ribs appear to have small uncinates. A series of dermal ossifications runs down the back from the head to well down the tail. These ossifications are arranged in pairs, one lying on each side of each vertebral spine and each has its long axis directed antero-posteriorly. A larger but less completely known genus has but a single large public foramen.

A third remarkable genus discovered by Brown has been named *Mesosuchus browni* by Watson. It is about the same size as *Euparkeria capensis* but differs in that while this latter has carnivorous Dinosaur-like teeth arranged in sockets, *Mesosuchus* has the teeth ankylosed to the bone and irregularly arranged on the maxilla. It also differs in a number of cranial characters, in the shape of the pelvis, and in the absence of dermal ossifications. Nevertheless it will probably have to be kept in the same order as *Euparkeria.*

The wonderful Permian and Triassic deposits of South Africa have in the Therocephalians, the Gorgonopsians, and the Cynodonts revealed to us practically the whole line of Mammalian descent, for in the Cynodonts we have types that are almost mammalian. In the Permian *Eunotosaurus* we probably have an ancestral Chelonian. In the Triassic *Paliguana* we have the oldest known Lacertilian. In *Proterosuchus*, *Euparkeria* and *Mesosuchus* we have representatives of an order which probably contained the ancestors of the Dinosaurs, the Pterodactyls, the Birds, and through *Erythrosuchus*-like types, of the Phytosaurs, and possibly of the Crocodiles.

Among Amphibians the most remarkable discovery has been two or three nearly perfect skeletons of our large South African *Eryops*-like form. It has been named *Myriodon senekalensis* by Van Hoepen, but it is almost certainly generically at least identical with the type previously described by me as *Rhinesuchus whaitsi.* Though a temnospondylous type it foreshadows in many characters the Cotylosaurs. Van Hoepen is shortly publishing a description of the remarkable skeleton.

A considerable number of new species and genera of fossil fishes from the Karroo are now known, but no strikingly new types.

Art. XLIX.—*The Melting Phenomena of the Plagioclase Feldspars*; by N. L. Bowen.

Introduction.

The exact relation which the feldspars, albite and anorthite, bear to each other has for a good many years been a question of much interest to mineralogists and petrologists. The continuous passage from the one to the other in chemical composition, found in the plagioclase feldspars, and the like passage in optical and other physical properties, has been regarded by the great majority as satisfactory evidence of complete solid solution. Since Day and Allen* added thermal properties to this list the evidence has been generally conceded to be conclusive.†

These investigators, working with chemically pure, artificial mixtures, studied the temperature of change of state from solid to liquid of various compositions under precisely similar conditions and were able to establish a perfectly continuous relation between them. The temperatures at which maximum heat absorption was found to occur, when plotted against composition, gave a smooth curve. The method used was not suitable for the determination of the magnitude of the melting interval or, more technically stated, the position of solidus and liquidus. The curve obtained by Day and Allen might, therefore, lie anywhere between the solidus and liquidus, and is not necessarily the liquidus itself, as some appear to have assumed. The attempt of Day and Allen to decide the question of a melting interval by trying to establish a difference of composition between the first crystals and the residue gave only negative results, but this fact, as they recognized,‡ might have been due to the extreme viscosity of the melts. Since the completion of this pioneer work of its kind, the facilities of the Geophysical Laboratory have been greatly increased, and one of the methods introduced (sudden cooling after long exposure to a fixed temperature) is especially useful for the study of melting phenomena in substances which form viscous liquids on melting. It was, therefore, deemed advisable to undertake the study of the plagioclase feldspars by this method of sudden quenching. The time consumed in the work was greatly les-

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* The Isomorphism and Thermal Properties of the Feldspars, Carnegie Institution of Washington, Pub. No. 31.

† Cf., however, Weinschenk-Clark, Petrographic Methods, New York, 1912, p. 331–332.

‡ L. c., p. 72.

sened by the fact that the writer was able to use in the present investigation the same artificial mixtures prepared by Day and Allen.

EXPERIMENTAL PART.

Method of Working.

An idea of the principle involved in quenching may be conveyed by a brief description of the method as practised. A charge of a given composition is held at a measured temperature for a definite period of time and is then quenched by allowing it to fall into a dish of mercury at room temperature. The instantaneous chilling precludes any possibility of physical or chemical readjustment in the charge; any portion that was liquid at the furnace temperature appears as glass, and any crystalline portion remains, in general, unchanged in crystal form. Examination of the quenched charge under the microscope, then, reveals those phases which were present at the furnace temperature. The time of holding the charge at constant temperature may be lengthened at will and equilibrium assured even in extremely viscous materials.

The furnace used in the present work was a platinum resistance furnace, kept at constant temperature by regulating a resistance in series with it. By constant watching, the temperature could be held within one degree of the temperature desired. The furnace thus becomes a high-temperature thermostat. The junction of the thermoelement was within seven or eight millimeters of the charge, which offered abundant accuracy in a thermostat arrangement.

This system (furnace and thermoelement) was calibrated by quenching charges of substances of known melting points, lithium metasilicate, diopside and anorthite, under like conditions. The results of this calibration are tabulated below. In each individual case the initial material was completely crystalline.

TABLE I.

Composition	Temperature microvolts	Time	Result	Date
Li_2SiO_3	11820	1/2 hr.	cryst.	Jan. 10, 1913
Li_2SiO_3	11920	1/2 hr.	cryst.	Jan. 10, 1913
Li_2SiO_3	11950	1/2 hr.	glass	Jan. 10, 1913
Li_2SiO_3	11950	1/4 hr.	glass	Jan. 10, 1913

The melting-point therefore lies between 11920 and 11950 microvolts; value by standard element 11953 microvolts. Correction to be applied to quenching system is therefore, for the present purpose, negligible.

$CaMg(SiO_3)_2$	14160	1/2 hr.	cryst.	Nov. 22, 1912
“ “	14200	1/2 hr.	glass	Nov. 22, 1912
“ “	14150	1/2 hr.	cryst.	Jan. 10, 1913
“ “	14180	1/2 hr.	glass	Jan. 10, 1913

Melting point between 14160 and 14180 M.V.
Value by standard element 14231 M.V. Correction + 60 M.V.

$CaAl_2Si_2O_8$	16100	1/2 hr.	glass	Nov. 22, 1912
“	16050	1/2 hr.	glass	Nov. 22, 1912
“	16010	1/2 hr.	cryst.	Nov. 22, 1913
“	16030	1/2 hr.	cryst. & glass	Jan. 10, 1913
“	16000	1/2 hr.	cryst. only	Jan. 10, 1913

Melting temperature 16030 M.V.
Value by standard element 16150 M.V. Correction + 120 M.V.

It will be noted that after several weeks continuous use (Nov. 22 to Jan. 10) the thermoelement was found unaltered. By interpolating between these values, the correction to be applied to the individual readings, in order to express them in terms of the standard element of Sosman and the nitrogen scale,* is readily found. These corrections have been applied to all readings in changing to degrees.

The application of this method of quenching to the specific problem of the feldspars was directed towards two definite ends; first, the determination of the exact limits of the melting interval for a given composition, and second, the determination of the composition of the solid and liquid phases present at a given temperature within the melting interval.

Determination of the Limits of the Melting Intervals.

The location of the temperature of the lower limit of the melting interval (solidus) was accomplished by starting with completely crystalline material of a certain composition and holding it for one hour at successively higher temperatures until a temperature was reached at which the quenched product showed a trace of glass. For the upper limit (liquidus), a charge wholly or partially crystalline was held at successively higher temperatures, again for periods of one hour each, until the quenched product showed that the last tiny crystals had dissolved in the glass. This temperature was then further checked by holding a clear glass of the same composition at successively lower temperatures until crystals appeared in the quenched product.

The results of these trials may be most concisely presented in tabular form.

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*This Journal, xxx, p. 1, 1910. Day and Sosman, High Temperature Gas Thermometry; Carnegie Institution of Washington, Pub. 157, p. 119.

TABLE II.

Date 1912	Initial Condition	Temp. microvolts	Temp. degrees.	Time	Result
Ab$_1$An$_5$					
Nov. 24	Cryst.	15110	1470	1 hr.	Small amount of glass formed.
Nov. 24	Cryst.	15000	1461	1 hr.	No change apparent.
Nov. 24	Cryst.	14900	1453	1 hr.	No change apparent.
Solidus 1465° ± 4°					
Nov. 26	Cryst.	15800	1530	½ hr.	All glass.
Nov. 26	Cryst.	15750	1526	½ hr.	All glass.
Nov. 26	Cryst.	15720	1522	½ hr.	All glass.
Nov. 27	Cryst.	15700	1520	1 hr.	Glass and a very few crystals.
Nov. 27	Glass	15650	1516	1 hr.	Glass and a very few crystals.
Liquidus 1521° ± 2°					
Ab$_1$An$_2$					
Nov. 22	Glass	15270	1484	1 hr.	Glass and a few crystals.
Nov. 22	Cryst.	15340	1489	1 hr.	Glass and crystal specks.
Nov. 22	Cryst.	15370	1492	1 hr.	Glass only.
1913					
Jan. 7	Cryst.	15300	1486	1 hr.	Glass and a few crystals.
Jan. 7	Cryst.	15350	1490	1 hr.	Glass only.
Liquidus 1490° ± 2°					
1912					
Nov. 23	Cryst.	13900	1368	1 hr.	No change.
Nov. 23	Cryst.	14010	1377	1 hr.	A very little glass formed.
Nov. 23	Cryst.	14200	1394	1 hr.	Glass formed.
Solidus 1372° ± 4°					
Ab$_1$An$_1$					
Dec. 8	Cryst.	13000	1291	1 hr.	Minute quantity glass.
Dec. 8	Cryst.	12900	1283	1 hr.	No change.
Dec. 12	Cryst.	13300	1316	1 hr.	Considerable amount of glass.
Solidus 1287° ± 4°					
Dec. 17	Cryst.	14650	1430	1 hr.	Glass and crystals.
Dec. 17	Cryst.	14770	1440	1 hr.	Glass and crystals.
Dec. 17	Cryst.	14800	1442	1 hr.	Glass and a few needle crystals.
Dec. 20	Glass	14800	1442	1 hr.	Glass and a few stout crystals.
Dec. 20	Cryst.	14870	1449	1 hr.	Glass and extremely rare crystals.
Dec. 20	Cryst.	14890	1452	1 hr.	Glass only.
Liquidus 1450° ± 2°					
Ab$_2$An$_1$					
1913					
Jan. 3	Cryst.	12600	1257°	1 hr.	Glass formed.
Jan. 3	Cryst.	12200	1223	1 hr.	Glass formed.
Jan. 8	Cryst.	12000	1209	1 hr.	Minute quantity glass.
Jan. 8	Cryst.	11900	1200	1 hr.	No glass discernible.
Solidus 1205° ± 5°					

TABLE II (continued).

Date 1912	Initial Condition	Temp. microvolts	Temp. degrees	Time	Result
			Ab_2An_1		
1912					
Dec. 19	Cryst.	14100	1386	1 hr.	Glass with a few crystals.
Dec. 24	Cryst. 1st preparation	14200	1394	1 hr.	Glass and crystal specks.
Dec. 24	Part cryst. 3d preparation	14200	1394	1 hr.	Glass and crystal specks.
Dec. 24	Diopside	14200	1394°	1 hr.	Glass only.
			Liquidus 1394° ± 2°		
			Ab_3An_1		
1913					
Jan. 7	Cryst. with	11690	1182	1 hr.	Slight increase of glass.
Jan. 7	trace glass	11550	1169	1 hr.	No change apparent.
			Solidus* 1175 ± 8°		
Jan. 9	Cryst.	13680	1349	1 hr.	Glass and a few crystals.
Jan. 9	Glass	13680	1349	1 hr.	Glass and a few crystals.
Jan. 9	Cryst.	13720	1352	1 hr.	Glass and rare crystals.
Jan. 10	Cryst.	13770	1356	1 hr.	Glass and very rare crystals.
Jan. 10	Cryst.	13820	1360	1 hr.	Glass and very rare crystals.
Jan. 10	Cryst.	13840	1363	1 hr.	All glass.
			Liquidus 1362° ± 2°		
			Ab_4An_1		
1912					
Dec. 17	Crystallized for one	13500	1332	1 hr.	Glass and extremely rare crystals.
Dec. 17	week, only partly	13410	1325	1 hr.	Glass and a few crystals.
Dec. 17	crystalline.	13530	1335	1 hr.	All glass.
			Liquidus 1334° ± 2°, solidus indeterminate.		
			Ab_8An_1		
1913					
Jan. 6	Partly cryst.	12580	1255	1 hr.	Glass and a few crystals.
Jan. 6	Partly cryst.	12600	1257	1 hr.	Glass and a few crystals.
Jan. 6	Partly cryst.	12680	1263	1½ hr.	Glass and rare crystals.
Jan. 6	Partly cryst.	12740	1268	½ hr.	Glass only.
			Liquidus 1265° ± 3°, solidus indeterminate.		
			Amelia County albite, $Ab_{98}An_2$		
Jan. 14	Cryst. coarse grains	10760	1102	1 hr.	No change.
Jan. 14	Cryst. coarse grains	11000	1122	1 hr.	A very little glass.

* Accuracy not quite as great as others on account of trace of glass in original.

TABLE II (continued).

Amelia County albite, $Ab_{98}An_2$.

Date 1913	Initial Condition.	Temp. microvolts	Temp. degrees	Time	Result
Jan. 14	Cryst. coarse grains	11130	1133	1 hr.	A very little glass.
Jan. 15	Cryst. coarse grains	11240	1143	2 hr.	Glass in stringers.
Jan. 15	Cryst. coarse grains	11440	1160	1 hr.	Glass in stringers.
Jan. 17	Cryst. fine powder	11450	1161	1 hr.	Much glass.
Jan. 18	Cryst. fine powder	11200	1140	1 hr.	Much glass.
Jan. 18	Cryst. fine powder	11000	1122	1 hr.	Glass in stringers.
Jan. 18	Cryst. fine powder	10800	1105	1 hr.	Glass in small stringers.
Jan. 18	Cryst. fine powder	10700	1097	2 hrs.	Doubtful slight change from original.
Jan. 18	Cryst. fine powder	10600	1089	2 hrs.	No change.

Beginning of melting 1100° ± 10°

Oligoclase from Bakersville, North Carolina.*

$Ab_{77.5}An_{22.5}$

Date 1913	Initial Condition.	Temp. microvolts	Temp. degrees	Time	Result
Jan. 15	Cryst.	11650	1175	1 hr.	Glass in stringers.
Jan. 15	Cryst.	11530	1165	1 hr.	A slight change.
Jan. 15	Cryst.	11420	1154	1 hr.	No change.

solidus 1158° ± 5°

Summary of Melting Intervals,

Composition.	Temperature of Beginning of Melting. Solidus.	Temperature of Completion of Melting. Liquidus.
An	1550° ± 2°	1550° ± 2°
Ab_1An_5	1465° ± 4°	1521° ± 2°
Ab_1An_2	1372° ± 4°	1490° ± 2°
Ab_1An_1	1287° ± 4°	1450° ± 2°
Ab_2An_1	1205° ± 5°	1394° ± 2°
Ab_3An_1	1175° ± 8°	1362° ± 2°
$Ab_{77.5}An_{22.5}$	1158° ± 5°	----------
Ab_4An_1	----------	1334° ± 2°
Ab_8An_1	----------	1265° ± 3°
$Ab_{98}An_2$	1100° ± 10°	----------

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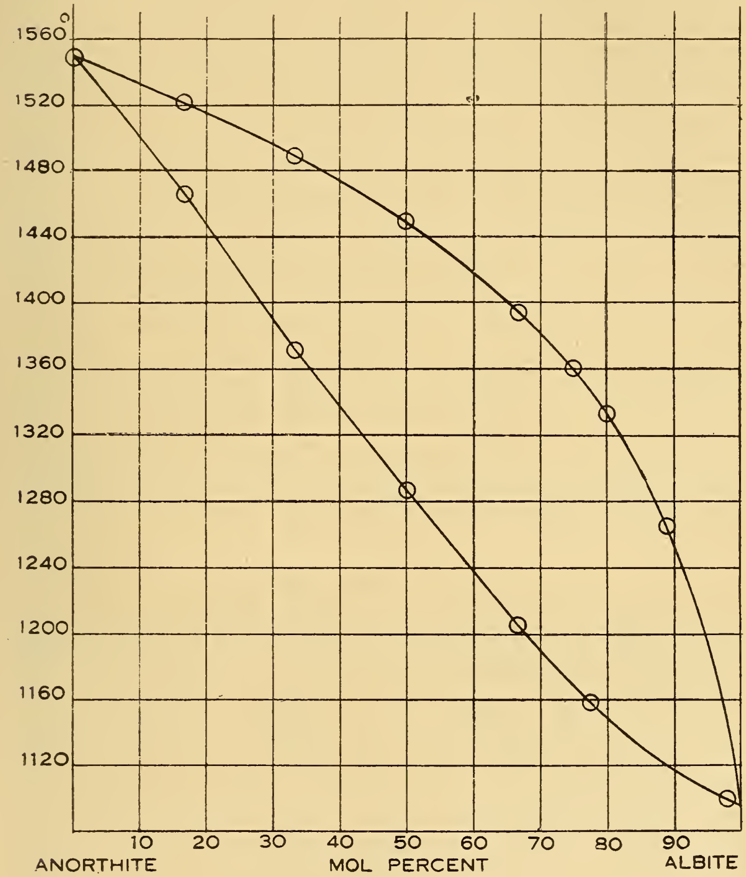
* Penfield and Sperry, this Journal (3), xxxvi, p. 324, 1888.

The data are shown plotted on a temperature-composition diagram in fig. 1. A clear idea of the extent and accuracy of the data on which the diagram rests may be obtained from Table II.

FIG. 1.



Order of Accuracy.

For the reason that it is somewhat easier to detect a few crystals embedded in glass than to find a small amount of glass in a crystalline aggregate, the accuracy of the liquidus is somewhat greater than that of the solidus. No difficulty was found, however, in establishing the solidus within limits of ± 4°.

The limits of error of the figures given for the liquidus (± 2°) are very accurately determined by ascertaining the temperature of the final disappearance of crystals. The check on these values by the reverse method of finding the temperature at which crystals first form in the glass was perfect, within approximately the same limits of error, in all the artificial mixtures except Ab_8An_1. It is possible to hold glass of this composition at a temperature a few degrees below the liquidus for several hours without the formation of crystals. No check on the liquidus point as determined by the reverse method was therefore possible in this case. That the point is sufficiently well established by the former method alone and with an accuracy practically equal to that in the more calcic members, is apparent, however, from the following. Beginning with half-crystalline material and holding it at 1263° for an hour and a half, it was found that a few rare crystals still persisted, whereas the same half-crystalline material held at 1268° (only 5° higher) for only half an hour gave a clear glass. It is obvious from the latter that the persistence of crystals at 1263° for an hour and a half could not have been due to insufficient time of exposure. In spite of the readiness with which under-cooling occurs, persistent superheating does not occur with this method of procedure. The importance of fixing the point on the liquidus corresponding to Ab_8An_1 is considerable because it determines the position and slope of the liquidus at a composition fairly close to albite itself.

Use of Natural Feldspars.

It was found impossible to *completely* crystallize pure artificial mixtures richer in albite than Ab_2An_1. The partially crystallized preparations as rich as Ab_8An_1, which were easily obtained, served perfectly well for fixing the liquidus, but, of course, were of no service in locating the solidus. A very pure natural oligoclase from Bakersville, North Carolina, of composition $Ab_{77.5}An_{22.5}$ was therefore used in an effort to fix the corresponding point on the solidus. A small portion of this material, carefully selected under the microscope, was finely ground and subjected to successive quenchings as before. The temperature of the beginning of melting was found to be 1158°±5°. (See Table II.)

For the same reason pure, natural material was also used to determine the melting point of albite. This Amelia County albite has been carefully analyzed* and found to contain about 2 per cent of anorthite and 1 per cent of orthoclase. What was really determined in this case also was the temperature of

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* Day and Allen, l. c., p. 48.

the beginning of melting of the mix crystals, for the presence of but 2 per cent of anorthite, on account of the steepness of the liquidus, is sufficient to cause a melting interval of about 50°. The temperature found for carefully selected, finely ground material was 1100°±10°. This may be taken as practically the melting temperature of albite itself on account of the flatness of the solidus at this point. In spite of the stubborn nature of albite in the matter of affording complete melting no great difficulty was found in fixing a temperature of beginning of melting of this material. The temperature 1100°, moreover, lies on a rational extrapolation of the liquidus, although extrapolation alone could not fix the point closely on account of the steep slope of the liquidus.

It will be noted that the curve of Day and Allen lies nowhere very far below the liquidus.* At Ab_2An_1 the difference is 20°. Beyond Ab_3An_1 no breaks were obtained by them and extrapolation was correspondingly uncertain.

The Composition of the Liquid Phase.

The composition of the phases present at any temperature could, of course, be predicted from the diagram as determined, but it was desired to obtain independent confirmation of it from actual determinations of optical properties. All hope of success in the case of the solid phase was soon abandoned, for the crystals, embedded in the glass, are always extremely small, sometimes so thin, in fact, that their birefringence is scarcely discernible.

In the case of the liquid phase the outlook was more hopeful, since the determination of a single property, viz., the refractive index of the glass, is sufficient to fix the composition. In most cases it was only when the glass was present in considerable excess over the crystals that its index could be determined, since it was only then that an edge of glass of sufficient size for comparison with the immersion liquid could be obtained. The difficulty was enhanced by the small size of the crystals embedded in the glass, for, on this account, five or six layers of crystals might be contained in the average grain and in the projection viewed under the microscope their apparent proportion was correspondingly multiplied. The difficulty was avoided in part by choosing only the thinnest grains, but this lessened somewhat the accuracy of the comparison with the liquid. In a few favorable instances, however, definite results were obtained.

To determine the refractive index the quenched charge was crushed and the fine powder† immersed in liquids of known

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* See revised temperatures, this Journal (4), xxxi, p. 347, 1911.

† Wright, F. E., The Methods of Petrographic-Microscopic Research, Carnegie Institution of Washington, Pub. No. 158, p. 87.

refractive index. By trying various mixtures one was readily found which exactly matched the glass, the comparison being made by the Becke line method. The index of the liquid was then immediately determined on the refractometer. The indices of the pure, artificial glasses of the albite-anorthite series had previously been determined at this laboratory by Larsen,[*] so that when the index was known the composition was also known.

The results obtained are tabulated below in such form as to indicate the extent of agreement of the two methods.

Table III.

Composition of charge Mol. % An.	Initial Condition.	Temperature.	Measured Index of glass.	Composition from index Mol. % An.	Composition from liquidus Mol. % An.
66·6 (Ab_1An_2)	Glass	1482°	1·542	63	63
	Glass	1462	>1·534<1·538	53·5—58	54·5
	Glass	1454	1·532	51	51·5
50·0 (Ab_1An_1)	Cryst.	1405	1·520	37	36
	Glass	1385	>1·514<1·518	30—35	31
	Glass	1432	1·525	43	44
33·3 (Ab_2An_1)	Cryst.	1324	1·506	20	19

By means of fig. 2 the composition of the liquid phase for each experiment, determined from its refractive index, may be quickly compared with the composition determined by the temperature method of fixing the liquidus. The agreement is excellent.

The temperature method is somewhat more accurate and much more generally applicable than the refractive index method. The latter, however, provides entirely independent confirmation of the former, and serves to demonstrate beyond doubt the great difference in composition between liquid and solid phases at any temperature. For example, a mixture of total composition Ab_1An_1 at 1385° gives a glass nearly 20 per cent richer in albite, and since about one-half of the charge is crystalline, it follows that the crystals must be approximately 20 per cent richer in anorthite. The actual difference between solidus and liquidus at 1385° is seen from fig. 1 to be 38 per cent.

From the zoned feldspars of nature it has long been known to geologists that a very considerable difference of this kind must exist. Vogt[†] has even ventured an estimate, for which he makes no claim of exactness, of the magnitude of this difference based on a comparison of the composition of the total

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[*] This Journal, xxviii, p. 283, 1909.

[†] T.M.P.M., xxiv, p. 514, 1905.

plagioclase of a rock, and that of the "first" plagioclase, but the actual determination of this magnitude has had to wait for the development of appropriate methods of measurement.

Fig. 2.

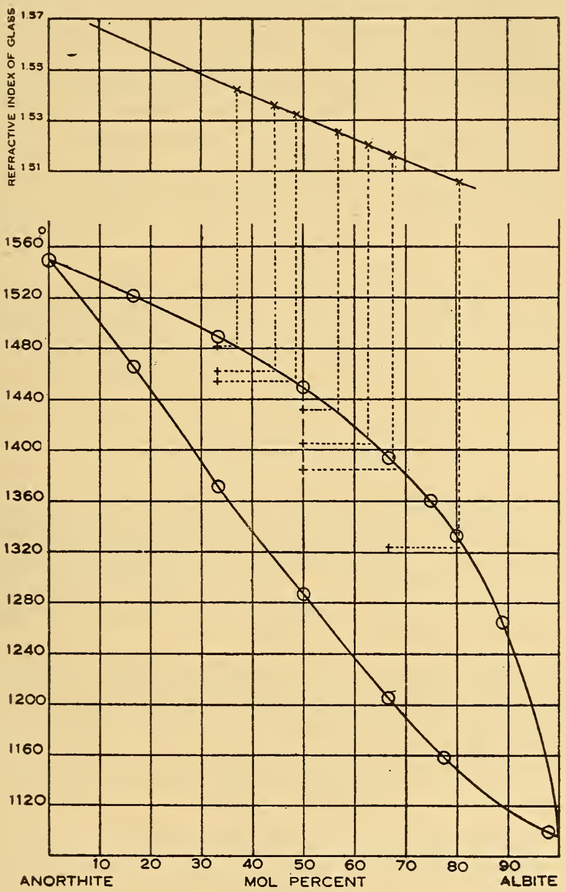

Fig. 2. + Total composition of charge and temperature of experiment.
× Determined refractive index of glass phase.

Theoretical Considerations.

Van Laar, in 1906, endeavored by means of a general equation, derived by consideration of the thermodynamic potential, to estimate the magnitude of the melting intervals of the plagioclase feldspars. He made use of the value of Day and

Allen for the melting point of anorthite (1532°) and the extrapolated value, 1220°, for albite, and with reasonable simplifying assumptions concerning the latent heats was able to show* that there should be large melting intervals.

For the case of complete solid solution of the type exhibited by the feldspars, we may derive equations expressing the relations between the composition of the liquid and solid in equilibrium at any temperature in the following manner. If both the liquid solutions and the solid solutions are *perfect physical solutions*, i. e., if there is no heat effect or volume change on mixing, then Raoult's law of vapor pressure lowering, and the Clausius equation for the change of vapor pressure with temperature, should apply to both components in both phases.

Raoult's law may be written in the following manner:

$$p = p_0\,(1 - x)$$

where p_0 = vapor pressure of the pure solvent at any temperature, and p = partial vapor pressure of the solvent at the same temperature, from a solution in which the mol fraction of solvent is $(1 - x)$.

The Clausius equation in its most general form is written

$$\frac{dp}{dT} = \frac{l}{(v_1 - v_2)T}$$

where dp is the change of vapor pressure of liquid (or solid) corresponding with a change of temperature dT at absolute temperature T, l = latent heat of vaporization of one gram of the liquid (or solid) at T, v_1 = the volume of one gram of the gas at T, and v_2 = the volume of one gram of liquid (or solid) at T.

By assuming that the gas laws apply to the vapor and that the volume of the liquid (or solid) is negligible compared with that of the gas, then the equation may be written in a form easily integrated.

$$\frac{d \log p}{dT} = \frac{L}{RT^2}$$

where L is the latent heat of vaporization of one mol. of the liquid (or solid) and R the gas constant. By assuming that L remains constant over the temperature range under consideration, we may integrate between the temperature limits T_1 and T_2, when the equation becomes

$$ln\,\frac{p_{T_1}}{p_{T_2}} = \frac{L}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

This, written in the exponential form, is the equation used in the present instance. Its complete derivation is given in order that the fundamental assumptions involved may be clear.

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* Zs. phys. Chemie, lv, 4, p. 435.

For component A let

p_o = vapor pressure of pure liquid at its melting point T_1 and therefore also the vapor pressure of pure solid at T_1.
$(p_o)_T$ = vapor pressure of pure liquid at T.
$(P_o)_T$ = vapor pressure of pure solid at T.
L_v = latent heat of vaporization of the liquid per mol at T.
L_s = latent heat of sublimation of the solid per mol at T.

then from the integrated Clausius equation the following relation holds for the liquid:

$$\frac{p_o}{(p_o)_T} = e^{\frac{L_v}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)}$$

and for the solid

$$\frac{p_o}{(P_o)_T} = e^{\frac{L_s}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)}$$

For a liquid solution of mol fraction $1 - x$, applying the Raoult's Law equation, we have then,

$$p_T = p_o \,.\, e^{\frac{L_v}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)} .(1 - x)$$

where p_T is the partial vapor pressure of A over the liquid solution at T.

For a solid solution of mol fraction $(1 - x_1)$ we have similarly

$$P_T = p_o \,.\, e^{\frac{L_s}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)} .(1 - x_1)$$

where P_T is the partial vapor pressure of A over the solid solution at T.

If T be the temperature at which this liquid solution and solid solution are in equilibrium, then $p_T = P_T$ and

$$p_o \,.\, e^{\frac{L_v}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)} \,.\, (1 - x) = p_o \,.\, e^{\frac{L_s}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)} \,.\, (1 - x_1)$$

whence $$\frac{1 - x}{1 - x_1} = e^{\frac{L_s - L_v}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)}$$

or $$\frac{1 - x}{1 - x_1} = e^{\frac{L_1}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)}$$

where L_1 = latent heat of melting (molal) of A at T.

By applying similar reasoning to component B we get

$$\frac{x}{x_1} = e^{\frac{L_2}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)}$$

where L_2 = latent heat of melting (molal) of B at T.

These two equations express the simultaneous concentrations on the liquidus and solidus at any temperature T in terms of the latent heats of melting at T and the temperatures of melting of the two components (T_1 and T_2).

Van Laar derives a more rigid relation which contains factors for the heats of mixing in both phases, but in its application he finds it necessary to neglect these and the equations then reduce substantially to the form given above.

In the present instance T_1 and T_2 and also the values for x and x_1 (the mol-fraction of albite on the liquidus and solidus curves respectively) for various values of T have been experimentally determined. (See fig. 1.) It suffices, then, in order to test the applicability of the equations in the case at hand, to substitute in the general equations and see whether or not L_1 and L_2 remain nearly constant and of appropriate order of magnitude. In the following table the calculated values are given:

Table IV.

$(T-273)$:	x observed:*	x_1 observed:	$1-x$ observed:	$1-x_1$ observed:	L_{Ab} calculated:	L_{An} calculated
1500	·277	·098	·723	·902	12670	28600
1450	·500	·192	·500	·808	12750	30000
1400	·651	·282	·349	·718	12790	29200
1350	·772	·376	·228	·624	12790	30400
1300	·846	·475	·154	·525	12470	28300
1250	·905	·575	·095	·425	12920	27700
	Mean				12740	29000
	Average deviation from mean,				0·8%	2·9%

It will be seen from the table that the values for the latent heats vary but little from a mean value, the random variation being what might be expected from the possible errors of the temperature measurements. Any systematic variation with temperature, due to the difference of specific heats of liquid and solid, would, by analogy with other silicates, be still smaller.†

If the calculated mean molal latent heat of melting of anorthite is divided by the formula weight, the result is 29000÷

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* See fig. 1.

† Cf. W. P. White, Specific heats of silicates and platinum, this Journal (4), xxviii, p. 345, 1909.

278 = 104·2. Åkerman and Vogt have found by direct measurement that the latent heat of melting of anorthite is 105 cal. per gram, which agrees well with the calculated value. The extraordinary agreement is, of course, in part pure accident. No direct determinations of the latent heat of melting of albite have been made. The value calculated from the present results is 12740 ÷ 263 = 48·5 cal. per gram, again using the formula weight.

FIG. 3.

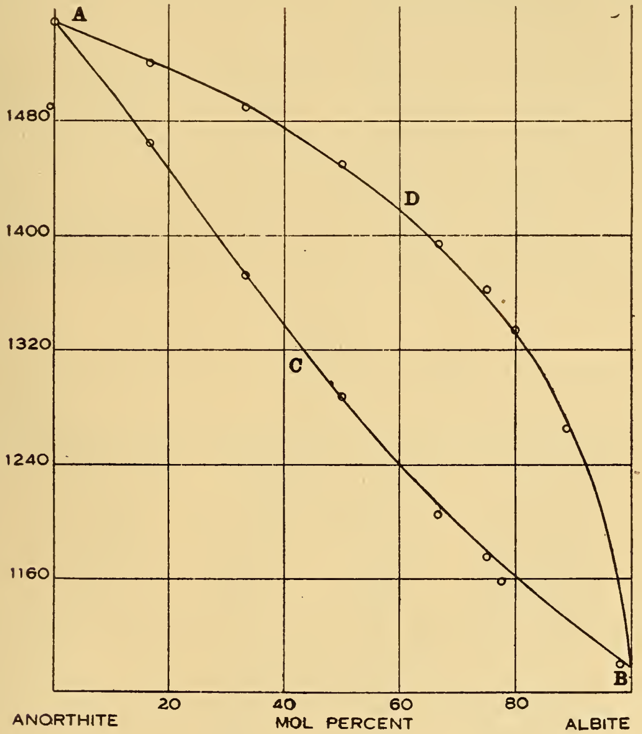

FIG. 3. ACB and ADB calculated curves (see text). o, experimentally determined points.

If the values 29000 and 12740 calories are taken as the molal latent heats of melting of anorthite and albite and the temperatures 1550° C. and 1100° C. as their melting points, complete solidus and liquidus curves can be calculated from these data. Actual calculation gives the curves ADB and ACB of fig. 3. The small circles of this figure indicate the experimentally determined temperatures. None of the determined points lies farther from the calculated curves than the possible limits of experimental error warrant. The greatest deviation occurs where the experimental errors are greatest.

Table V is given in order to show that this agreement is clearly not fortuitous and that no values of the latent heats except those very close to the calculated values will give curves that pass near enough to the experimentally determined points to permit the interpretation that the deviation of the points is due to experimental error.

The table gives the temperatures of some points on liquidus and solidus curves calculated by the use of values of the latent heats differing 10 per cent from the mean values 12740 and 29000 calories. The latent heats are allowed to vary from the mean values both separately and jointly and, in the latter case, both in the same direction and in opposite directions. In each case the differences between the calculated and observed temperatures are well beyond the limits of error of the temperature measurements. The observed temperatures, therefore, fix closely the values of L_{An} and L_{Ab}.

TABLE V.

Case I.

Assuming a value of L_{Ab} 10 per cent lower than above mean value and a value of L_{An} equal to above mean value

Point on Solidus.

Composition	Calculated	Observed	Difference
Ab_1An_5	1475°	1465°	+10°
Ab_1An_2	1390°	1372°	+18°
Ab_1An_1	1305°	1287°	+18°

Point on Liquidus.

Composition	Calculated	Observed	Difference
Ab_1An_2	1493°	1490°	+3°
Ab_1An_1	1454°	1450°	+4°
Ab_2An_1	1400°	1394°	+6°

Case II.

Assuming a value of L_{Ab} equal to above mean value and a value of L_{An} 10 per cent less than mean value

Point on Solidus.

Composition	Calculated	Observed	Difference
Ab_1An_5	1458°	1465°	−7°
Ab_1An_2	1363°	1372°	−9°

Point on Liquidus.

Ab_1An_5	1517°	1521°	$-4°$
Ab_1An_2	1480°	1490°	$-10°$
Ab_1An_1	1436°	1450°	$-14°$
Ab_2An_1	1380°	1394°	$-14°$

Case III.

Assuming a value of L_{Ab} 10 per cent lower than above mean value and a value of L_{An} 10 per cent lower than above mean value

Point on Solidus.

Composition	Calculated	Observed	Difference
Ab_1An_2	1382°	1372°	$+10°$
Ab_1An_1	1299°	1287°	$+12°$
	Point on Liquidus.		
Ab_1An_2	1485°	1490°	$-5°$
Ab_1An_1	1441°	1450°	$-9°$
Ab_2An_1	1386°	1394°	$-8°$

Case IV.

Assuming a value of L_{Ab} 10 per cent higher than above mean value and a value of L_{An} 10 per cent lower than above mean value

Point on Solidus.

Composition	Calculated	Observed	Difference
Ab_1An_2	1350°	1372°	$-22°$
	Point on Liquidus.		
Ab_1An_1	1430°	1450°	$-20°$

The marked accord between theory and the measurements here offered is, on first thought, rather surprising. We are not dealing simply with dilute solutions, nor is the solid which separates the pure solvent, and it is commonly only in such cases that measurements of freezing point lowering are found amenable to simple laws. It should be noted, however, that the equations applied have the general form applicable to all solutions and not merely to the limiting case of the dilute solution. Moreover, the fundamental assumption in the derivation was that both the liquid solutions and the solid solutions followed Raoult's law of vapor pressure lowering. This law is well known to be applicable to many pairs of liquids, for all concentrations, when these liquids are miscible in all proportions and when there is neither volume change nor heat effect on mixing. The feldspar liquids fulfill the first two requirements. The density of the feldspar glasses at room temperature is nearly linear with respect to composition and at higher temperatures this relation probably does not change to any great extent.* Of the heat effect on mixing, nothing is known, but it seems that two such similar substances might prove analogous to members of the same homologous series among organic liquids, and that no great effect need be expected.

Turning to the solids, we find the same facts true. They are miscible in all proportions and again the change of density with composition is linear. It would seem, then, on more mature thought, that we are dealing with an especially favorable case, and that Raoult's law might be expected to apply to both phases. This is indeed what has been found.

In the case of solids not completely miscible, it is easy to prove that *both* saturated solid solutions can not obey Raoult's law, i. e., if one does the other can not. In the case, therefore, of two series of mix-crystals with an hiatus, and especially when this hiatus is so large that the two components separate in the pure state, it does not appear possible that any rule of freezing-point lowering, derived from the considerations set forth in the present derivation, would be found to apply.†

The close agreement found between observation and theory points to other important conclusions relative to these components. One is that albite and anorthite, both in the liquid and solid state, consist of simple molecules, or else that they are equally associated and that the degree of association is not affected by mixing them. This follows from the fact that, in plotting mol fractions (mol. percentages), molecular weights were assumed equal to formula weights. If they had been assumed to be equal multiples of the formula weights, the plot would have been, of course, exactly the same. It might be assumed that since L (calculated) for anorthite is found to be equal to the experimentally determined latent heat per gram multiplied by the formula weight, that the molecule is necessarily simple, but L is merely the difference between the heats of vaporization and of sublimation of a mol and refers therefore only to the gas mol. It is a constant characteristic of the substance and in the present instance it is easy to see that, whether simple or equally associated molecules are assumed in its calculation, its value remains the same. The experimental results do not, therefore, throw any light on the actual degree of association of albite and anorthite. They indicate, as pointed out, that each is equally associated in the solid state and also in the liquid state, though the association may be, and probably is, different in the different states.

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* Day and Allen, l. c., p. 71.

† Cf. E. W. Washburn, J. Am. Chem. Soc., xxxii, No. 5, May, 1910, p. 670, for liquids.

The Question of Küster's Rule.

Both the equations derived and the decisive nature of the experimental results demonstrate that Küster's rule* can apply only in a certain limiting case. This rule states that the melting points of isomorphous mixtures should lie on the straight line joining the melting points of the pure components. It can be seen from inspection of the equations for the liquidus and solidus that the two curves may lie close together if either L_1 or L_2 is very small, and that both may approach straight lines if both L_1 and L_2 are small, but that they can not become a single straight line unless $T_1 = T_2$, i. e., the difference between the melting points of the components, is zero.† That vapor pressures, densities and like properties, when measured *at a definite temperature*, should be linear with respect to composition for solid solutions which are perfect physical solutions, is a necessity. That such a rule should apply to melting points, themselves *variable temperatures*, does not follow.

Isomorphism.

The establishment of complete solid solution between the feldspars raises the whole question of the use of the terms "solid solution" and "isomorphism." The latter has been avoided hitherto in this paper on account of the variety of meanings which have at different times been attached to it. Some authors use "isomorphism" to designate complete solid solution, others speak freely of "limited isomorphism," and still others use the term in its original significance of simple crystallographic similarity, without regard to the question of miscibility in the solid state. In view of the recent very complete review of the subject by Hlawatsch,‡ nothing more need be said of this matter except that, for the conception of miscibility in the solid state, the term, solid solution, seems to be much more useful, both in avoiding ambiguity, and because of a certain connotation of similarity with liquid solutions which has been amply justified in the present instance.

It has hitherto proved impossible to agree upon a deciding factor which shall determine whether or not two substances shall form a complete series of solid solutions. The facts indicate rather that no *single* criterion may be safely used alone. Similarity of chemical composition, for example, is known to be favorable. Except that both are alumino-silicates, no great similarity of composition between albite and anorthite, as their formulæ are ordinarily written, can be claimed. For this

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* F. W. Küster, Zs. phys. Chem., viii, p. 577, 1891.

† Cf. Van Laar, loc. cit., p. 439, and Day and Allen, loc. cit., p. 68.

‡ Zs. Kryst., li, p. 417, 1912.

reason a rearrangement of the formulæ has been proposed by Washington* to enable both to be written as salts of the same acid, with, as far as present knowledge goes, extremely dissimilar basic radicles.

It is not, however, clear that a common acid radicle is more favorable to complete miscibility than a common basic radicle, for the pair $CdBr_2 - CdI_2$, and also the pair $K_2CrO_4 - K_2SO_4$, form complete series of solid solutions. These facts, of course, prove nothing relative to the feldspars, but they indicate that, until more is known of the laws of miscibility in the solid state, there is no compelling need to assume that albite and anorthite are salts of the same acid.

It has been shown in some cases that crystalline similarity alone, even when very marked,† may not be sufficient to determine miscibility in the solid state, but that the molecular volumes of the two substances must also be nearly equal, or, stated in another form, the fundamental structural parallelopipeda must be alike not only in shape but also in size. It happens in the present case that the molecular volumes are nearly identical and it may, therefore, be in part due to this fact that complete miscibility is possible. The molecular volume is equal to the molecular weight divided by the density, but since in general nothing is known of the molecular weight of the solid, the molecular volume is equally indefinite. The melting phenomena have shown, however, in the present case, that in the solid state albite and anorthite consist either of simple or of equally associated molecules. The molecular volumes, calculated on the assumption that the molecules are simple, will therefore give figures which represent the actual ratio of these quantities. The molecular volume of anorthite, so calculated, is $\frac{278 \cdot 9}{2 \cdot 765} = 100 \cdot 8$ and of albite $\frac{263 \cdot 0}{2 \cdot 605} = 100 \cdot 9$, practically identical values.

Of the still more fundamental question as to the factor which determines the crystallographic similarity and therefore, ultimately, the complete miscibility there is very little positive knowledge. It may be noted, however, that the valency-volume theory of Barlow and Pope‡ is applicable to the present pair, inasmuch as they have the same valency volume (32) and could be derived from related, closely-packed assemblages of spheres of atomic influence.

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* This Journal, xxxiv, p. 555, 1912.

† Tutton, A. E. H., Crystalline Structure and Chemical Constitution, p. 128, London, 1910.

‡ Jour. Chem. Soc., lxxxix, p. 1727, 1906.

GEOLOGICAL SIGNIFICANCE.

A study of fig. 1 brings out certain facts concerning the plagioclases which seem worthy of some attention. If we start with a mixture of composition Ab_1An_1 at 1500° and cool quickly, crystallization may not begin until some such temperature as 1250° is reached, when the whole will solidify as homogeneous crystals of Ab_1An_1.

If we cool gradually, on the other hand, crystals of composition $Ab_{19}An_{81}$ begin to separate at 1450° and, theoretically, the composition of the crystals will change continuously toward Ab_1An_1 and their amount will increase down to 1287°, when the whole mass will consist of crystals of composition Ab_1An_1. This continuous complete change in the composition of the solid implies, however, free diffusion in the solid phase, whereas diffusion is in general quite slow in solids and in the feldspars is certainly extremely slow. Only excessively slow cooling could therefore be expected to give the result outlined. With moderately slow cooling the process consists in the formation of successive layers of crystalline material of gradually changing composition, the early layers being effectively separated from the liquid by the later. When the temperature 1287° is reached, there will still be some liquid left. Crystallization will therefore continue below this temperature, the process of gradual change of composition in the solid deposited and the liquid residue continuing as before. *If the cooling is at the proper rate, there appears to be no limit to this process ; the final crystals may be nearly pure albite.*

This may be illustrated by a precise numerical example. Start with 100 grams Ab_1An_1 at 1500° and cool it instantaneously to 1386°. At this temperature 50 g. of crystals, $Ab_{31}An_{69}$, will separate and 50 g. of liquid, $Ab_{69}An_{31}$, will remain. (See fig. 1.) Cool again instantaneously to 1282°, 25 g. of crystals, $Ab_{51}An_{49}$, separate and 25 g. of liquid, $Ab_{87}An_{13}$, remain. Again, repeat the cooling and at 1164° 12·5 g. of crystals, $Ab_{76}An_{24}$, form and 12·5 g. of liquid, $Ab_{98.5}An_{1.5}$, remain. It is easy to see how by continuous slow cooling, instead of cooling in steps, the same result might be obtained and that the final crystals might approach pure albite. Absolutely pure albite, however, could not be obtained in finite amount. Moreover, the temperature may fall to 1100° before crystallization is complete.

It is believed that this very large range of temperature through which the crystallization of plagioclase may take place, with moderately slow cooling, is of great importance in igneous geology. Such a behavior may sometimes be favored in the natural rocks, even when cooled exceedingly slowly, on account of the possibility that the liquid may be separated from the crystals, say by the sinking of the latter or by reintrusion of the former to a higher level. The actual temperatures concerned will, of course, be much lower in the natural rocks.

The reversal* of the order of zoning sometimes noted in natural plagioclase may perhaps result from various causes. That undercooling might bring about a reversal may be seen from inspection of fig. 1. If liquid of composition Ab_1An_1 were cooled quickly to 1280°, rapid formation of crystals (Ab_1An_1) might take place at this temperature, and the heat (latent) released might quickly raise the temperature of the whole mixture to 1300°, at which temperature a zone of crystalline material of composition $Ab_{45}An_{55}$ would form around the earlier less calcic crystals. Similar undercooling might bring about a like result in a natural magma.

The secret of reversal may at times be found in the presence of other lime-bearing minerals in the natural rock. Movement of the magma during crystallization might bring about the same result by exposing the crystals to liquid of composition different from that out of which they had been crystallizing. To such movements also, and perhaps, at times, to sudden lowering of temperature, may be attributed the sharp boundaries that various zones often exhibit.

In view of the very great quantitative importance of the plagioclases in igneous rocks, it is a matter of some satisfaction to find them obeying the laws of physical chemistry to the extent here found.

SUMMARY.

The method of quenching was applied to the determination of the melting intervals of pure, artificial plagioclase feldspars. It was found possible to determine accurately the temperatures of beginning of melting (solidus) for compositions ranging from pure An to Ab_3An_1, and of completion of melting (liquidus) for the range $An-Ab_8An_1$. Very pure natural material, Bakersville oligoclase, was used to determine the point on the solidus corresponding to its composition. Similar material, Amelia County albite, served to fix the melting point of albite. The results of this work are summarized at the end of Table II and diagrammatically expressed in fig. 1.

It was also found possible in several instances to determine the composition of the liquid phase, present at temperatures within the melting interval, by measuring the refractive index of the quenched glass. Thus points on the liquidus were determined by an independent method and were found to be

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* N. L. Bowen, J. Geol., xviii, p. 662, 1910.

in excellent agreement with the results of the temperature method. In Table III and fig. 2 the results are shown.

In the theoretical discussion equations are developed which express the concentrations on the liquidus and solidus at any temperature in terms of the melting temperatures and latent heats of melting of the two components. The experimental results therefore make possible the calculation of the latent heat of melting of anorthite and of albite. The calculated values are 104·2 cal. per gm. for anorthite and 48·5 cal. per gm. for albite and these values remain practically constant for all ranges of composition (see Table IV). The calculated latent heat of anorthite is in excellent agreement with the figure found by direct measurement, 105 cal. per gm. No direct determinations of the latent heat of albite have been made.

It is shown that if these values of the latent heats are taken and liquidus and solidus curves calculated, the resulting curves (see fig. 3) pass very close to the experimentally determined temperatures (within the limits of error of the temperature measurements). It is also shown that values of the latent heats differing from these by as little as 10 per cent will not give a like result. (Table V.)

This extreme agreement with the requirements of theory and its bearing on certain theoretical questions is discussed.

The geological significance of the complete solid solution of the feldspars is considered, as well as the extent to which zoning may occur under favorable conditions and the consequent very great range of temperature through which plagioclase may crystallize.

Geophysical Laboratory,
Carnegie Institution of Washington,
Washington, D. C., March, 1913.

Art. L.—*On Hetærolite from Leadville, Colorado;* by W. E. Ford and W. M. Bradley.

In November, 1911, a small specimen of a zinc-manganese oxide, coming from the Wolftone Mine at Leadville, Colorado, was sent to Prof. E. S. Dana by Mr. W. C. Wetherill, at that time consulting engineer for the Empire Zinc Company. In the letter that accompanied the specimen was a copy of a preliminary analysis of the mineral made by Mr. Glenn Haigh for the company. This analysis, together with the physical properties of the mineral, indicated that it might be a new species. Prof. Dana kindly turned the matter over to the Mineralogical Laboratory of the Sheffield Scientific School for examination. Unfortunately Mr. Wetherill died before an opportunity offered to carry out the investigation. Later, in May, 1912, Dr. William S. Ward, curator of the Mineral Collection in the Colorado Museum of Natural History in Denver, wrote further about the matter and generously donated a fine specimen of the mineral. Mr. Wetherill originally suggested that, if the substance proved to be a new species, it be named after the property on which it was found; Dr. Ward, in his letter, made the counter suggestion that it be named after Mr. Wetherill, who first called attention to it. On detailed examination, however, the mineral has proved to be identical with hetærolite, previously described from Stirling Hill, Sussex County, N. J., and consequently both of these suggestions have had to be disregarded.

Hetærolite was first described in 1877 by Dr. Gideon E. Moore in a brief notice published in this Journal.* The essential points of his description follow: It was found in an ochreous limonite with chalcophanite. It occurred in botryoidal coatings of columnar radiating structure. Its hardness was 5, and its specific gravity 4·933. Its luster, metallic to submetallic; color, black; streak, brownish black. It was infusible; in the closed tube it gave a little water; with fluxes it gave the reactions for manganese and zinc. No analysis was quoted, but the statement was made that the formula was that of a zinc hausmannite, $ZnO.Mn_2O_3$.

Because of the incomplete description, the mineral has been considered a doubtful species, and was placed by Dana in the System of Mineralogy in the Appendix to Oxides.† In 1910, Prof. Charles Palache published an analysis‡ made in 1906 by

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* This Journal, xiv, 423, 1877.

† System of Mineralogy, 6th ed., p. 259, 1892.

‡ This Journal, xxix, 180, 1910.

W. T. Schaller, of material from the original locality. This analysis was considered to confirm Moore's formula, and to establish the mineral as a distinct species. The mineral was stated, in this article, to be tetragonal, as shown by the optical behavior of the fibers under the microscope, and to have an indistinct prismatic cleavage. Specific gravity was given as 4·85. The analysis by Schaller is quoted in a later paragraph.

The hetærolite from Leadville was found on the Woftone property, at a depth of about 700 feet below the surface. It occurs as an occasional vug-filling mineral at the lower contact of the blue limestone with a quartzite. It is associated with calamine crystals and with smithonite. It has a radiating, mammillary structure. In general, the outer surfaces are smooth and rounded, but in one cavity of the specimen they are covered with a drusy coating of microscopic crystals. These are much too small, however, to admit of any measurements being made. When broken the radiating masses show a prismatic structure similar to that observed on many specimens of gœthite and manganite. Under the microscope, the very fine fragments become transparent, having a dark brown color. They show birefringence and have an extinction parallel to the prismatic edges. No further evidence of its crystal system could be discovered. The index of refraction was determined to be greater than 1·78, by noting the effect upon the small fragments when immersed in a liquid having this index of refraction.

The mineral shows a splintery fracture. Its hardness is between 5·5 and 6. The specific gravity was determined as 4·6. Its luster is submetallic. Its color is dark brownish to black, with often a bright varnish-like exterior. It gives a dark chocolate-brown streak.

It is infusible. On charcoal with sodium carbonate it gives the characteristic zinc oxide coating. With the fluxes it gives the color reactions indicative of manganese. It is easily soluble in hydrochloric acid, giving off chlorine gas. It yields water when heated in the closed tube, but does not give off oxygen gas.

The method of analysis was briefly as follows: The water was determined by the direct method of Penfield.* The residue from this determination was dissolved in hydrochloric acid and silica determined as usual. The filtrate from the insoluble silica was evaporated to dryness in order to remove the hydrochloric acid. The residue was dissolved in about 200^{cc} of water. To this 50^{cc} of formic acid was added and an aqueous solution of about 3 grams of sodium acetate. This solution was warmed to about 60° C. and the zinc precipitated by

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* This Journal, xlviii, 31, 1894.

hydrogen sulphide gas. The precipitate was filtered upon an asbestos mat in a filter tube† and ignited in a current of hydrogen sulphide. The filtrate from the zinc precipitate was boiled to remove the hydrogen sulphide and then an excess of bromine water and ammonium hydroxide was added. The resulting manganese dioxide precipitate was filtered off, dissolved by hot sulphur dioxide water and the manganese reprecipitated by hydrogen sodium phosphate and finally weighed as manganese pyrophosphate. The available oxygen was determined by the oxalic acid method.

The results of the analyses by Bradley follow. The partial analysis by Haigh is also given in the last column.

	I	II	Average	Ratios	Anal. by Haigh
ZnO	37·41	37·70	37·56	0·461	37·1
MnO	50·29	50·39	50·34	0·709	45·9
O	5·99	5·99	5·99	0·374	5·9
CaO	trace	trace	trace		
H_2O	4·37	4·36	4·36	0·242	4·7
SiO_2	2·69	2·70	2·69	0·044	Insol. 2·0
	100·75	101·14	100·94		
Mn_2O_3	55·95	56·06	56·00	0·354	

Ignoring for the present the small amount of silica shown by the analysis, the molecular ratios have the following relations: The manganese protoxide is to the available oxygen as 0·709 : 0·374 or as 2·00 : 1·05. Evidently, the manganese is present in the mineral as the sesquioxide, Mn_2O_3. This assumption is borne out by the facts that although the manganese is in the form of a higher oxide, since there is an excess of oxygen present, it cannot be in the form of the dioxide because when the mineral is heated in the closed tube there is no oxygen liberated. The percentages of Mn_2O_3, calculated from the amounts of MnO that were found, are given above. On this assumption the ratios become $ZnO : Mn_2O_3 : H_2O =$ 0·461 : 0·354 : 0·242 or as 1 : 0·76 : 0·52. These results might be taken to indicate that the formula of the mineral was $4ZnO.3Mn_2O_3.2H_2O$.

It seems, however, impossible to neglect the presence of the silica. As this exists in a soluble form, it is probably present as a definite mineral molecule. As the hetærolite is intimately associated in its occurrence with calamine, it is reasonable to suppose that the silica is present as a part of that mineral. The physical structure of the material analyzed was

* This Journal, xxi, 453, 1906.

such as to make it very probable that this might be the case. If all the silica present is considered to occur as a part of the calamine molecule, it means that about ten per cent of the material analyzed was that mineral. It is recognized that this is a large amount to be present and still escape discovery, but it is thought that the fibrous structure of the hetærolite might very well serve to conceal this amount. The calculations below have been made on this assumption, sufficient amounts of zinc oxide and water being subtracted to form with the silica the calamine molecule, $H_2O.2ZnO.SiO_2$.

		Subtracting the equivalent of $H_2O.2ZnO.SiO_2$		Reduced to 100 per cent	Ratios	
ZnO	37·56	− 7·25	= 30·31	33·73	0·414	= 1·00
Mn_2O_3	56·00		56·00	62·32	0·394	= 0·95
H_2O	4·36	− 0·81	= 3·55	3·95	0·219	= 0·52
SiO_2	2·69	− 2·69				
	100·61		89·86	100·00		

If the above reasoning is correct, the formula becomes quite clearly $2ZnO.2Mn_2O_3.1H_2O$. The theoretical composition derived from this formula is as follows:

	Theory
ZnO	32·78
Mn_2O_3	63·60
H_2O	3·62
	100·00

The analysis by Schaller, which was quoted by Palache, is given below:

	1	2	Ratios	
ZnO	33·43	35·32	0·435	1·06
Mn_2O_3	60·44	63·85	0·405	1·00
Fe_2O_3	0·77	0·83	0·005	
SiO_2	1·71			
H_2O-	2·47			
H_2O+	1·42			
	100·24	100·00		

In the calculations given above the silica is disregarded and no statement is made in the original discussion as to its probable nature. The 3·89 per cent of water is also dismissed as "probably contained in a slight admixture of chalcophanite." To the present writers it does not seem as if the water at least could be so easily eliminated from the analysis. At any rate the explanation of the probable cause of its presence seems to be untenable. Chalcophanite contains, theoretically, 12·5 per cent of water. Consequently, if the 3·89 per cent of water given in the above analysis was due to admixture of chalcophanite, nearly one-third of the material analyzed must have been that mineral. Further, over 9 per cent of manganese dioxide derived from that amount of chalcophanite would also have been present. If the water found is included in the analysis, the following composition and ratios are derived:

ZnO	33·93	0·416		2·00
Mn_2O_3	61·24	0·388	0·392	1·88
Fe_2O_3	0·78	0·004		
H_2O	3·95	0·220		1·05
	100·00			

The formula derived from the above calculation is the same as that derived from the analysis of the Leadville mineral. Whatever the correct interpretation of the analyses may be, it is certain that the specimens from the two localities are to be considered the same chemically. Prof. Palache kindly sent to us a specimen of the Stirling Hill material for comparison, and it agrees perfectly with the Leadville mineral in all physical and optical tests. It may be that the exact composition of hetærolite cannot be definitely settled until purer material can be analyzed. With the evidence at hand, however, the present writers prefer to include the water as an essential part of the composition, making the formula $2ZnO.2Mn_2O_3.1H_2O$.

Mineralogical Laboratory of the Sheffield Scientific School
of Yale University, New Haven, Conn.,
March 11, 1913.

Art. LI.—*On the Hydrolysis of Esters of Substituted Aliphatic Acids;* by E. W. Dean.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxlv.]

6. Saponification by Sodium Hydroxide of Hydroxy and Alkyloxy Acetates and Propionates.

General Discussion.

Having recently determined the velocity constants of several esters for their hydrolysis in decinormal acid, it was decided to continue the study by measurements taken in alkaline solution.

Considerable work has been done in this line in connection with the theory of steric hindrance and some of the esters in the list included in this paper have been examined before. Brief mention is made of the researches which have more or less important bearing upon the experiments here described.

The velocity of saponification of ethyl acetate seems to have been measured first by Warder.* Soon after came a series of very accurate and comprehensive measurements by Reicher.† He determined the relative effects of various bases and also showed that the effect of the alcohol radical in the ester is practically constant. Methyl esters decompose most rapidly and the velocity decreases up the series. The differences, however, are exceedingly slight beyond about the first three members. Reicher's experiments with the esters of different acids pointed toward a decrease in velocity with increasing molecular weight.

The effect of the presence of neutral salts on the velocity of saponification has been studied by Arrhenius‡ and by Armstrong and Watson.§ Measurements have been made by Hjelt‖ on esters of polybasic acids and by Goldschmidt¶ on acetacetic ester. The most important work in the present connection is that of Findlay and Turner** and Findlay and Hickmans.†† Here careful determinations have been made of the effect of hydroxyl and alkyloxyl groups on the velocity of reaction. In two cases the esters saponified have been included in the series considered in this paper. The results of this work will be taken up in detail later.

Preparation of Material.

The esters used were in general portions of the same samples hydrolyzed in acid solution, results of which work‡‡ have been

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* Ber., xiv, 1361.

† Ann., ccxxviii, 251.

‡ Zeitschr. phys. Chem., i, 110.

§ Proc. Royal Soc., Series A, lxxix, 564.

‖ Ber., xxix, 110; xxxi, 1844.

¶ Ibid., xxxii, 3396.

** Jour. Chem. Soc., lxxxvii, 747.

†† Ibid., xcv, 1004.

‡‡ This Journal, xxxiv, 293.

fully described. The list included ethyl acetate, ethyl glycollate, three alkyloxy acetates, ethyl propionate, ethyl lactate, and ethyl alpha and beta ethyloxy propionates. The methods of preparation and properties of these esters need no discussion here.

Solutions of hundredth normal barium hydroxide and approximately fortieth normal sodium hydroxide were prepared free from carbonate by the usual methods. Hundredth normal hydrochloric acid was prepared and standardized by silver precipitation.

Procedure.

Measurements were made of reactions at two temperatures, zero degrees and twenty-five degrees. For the former series was used a small thermostat filled with ice and water and vigorously stirred. A temperature constant within a tenth of a degree was easily maintained in this manner. For work at twenty-five degrees the thermostat fully described in a previous paper* was employed.

The actual experiments were carried on by a slight modification of the method recommended by Ostwald.† In the thermostat were placed two flasks, one containing a measured amount of fortieth normal sodium hydroxide solution, the other a solution of the ester of slightly smaller concentration than that of the alkali. At the proper time an amount of the ester solution equal to that taken of the sodium hydroxide was withdrawn by means of a pipette and allowed to flow rapidly into the reaction flask. This was shaken vigorously, replaced in the thermostat and a ten cubic centimeter portion removed and allowed to run into a known quantity (15^{cm^3}) of hundredth normal hydrochloric acid. The excess of acid was then determined by titration with centinormal barium hydroxide. Rosolic acid was used as an indicator, this having been proven by experience to be better than phenolphthalein under the conditions described.

To obtain good constants by the method thus described requires a moderate amount of skill in manipulation. We are at present unable to compare its advantages with those of the conductivity method of Walker,‡ employed by Findlay and Hickmans.§ We therefore limit ourselves to stating the sources of error and the precautions adopted. In order to be able to check the reaction abruptly at the end of any interval of time, a pipette which discharged the major portion of its contents in four or five seconds was used. By vigorously rotating the flask into which the pipette was emptied the alkali was

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* This Journal, xxx, 72.

† Ostwald-Luther, Physiko-Chemische Messungen. 3d ed., p. 529.

‡ Proc. Roy. Soc., Series A., lxxviii, 157.

§ Loc. cit.

immediately neutralized by the excess of acid present. In this way a very sharp end-point was obtained, since in acid of such dilution the velocity of decomposition of any ester is negligible. It seems probable that irregularities in constants caused in this way are very slight, especially in view of the fact that uniform procedure was adopted for all measurements. The principal cause of irregularities is the difficulty of titrating accurately with such dilute solutions in the presence of relatively large amounts of salts of the organic acids. On the whole, however, reasonably good constants were obtained even in cases where the reaction proceeded with considerable velocity.

Calculations were made by the use of the titration formula* for reactions of the second order.

$$K = \frac{1}{\cdot 4343 \cdot t \cdot T_\infty} \cdot \frac{V}{n} \cdot [\log T + \log (T_0 - T_\infty) - \log T_0 - \log (T - T_0)]$$

T is the amount of HCl consumed by the excess of NaOH at the time *t*. T_0 is the initial titration and T_x the titration value of the excess of NaOH at the end of the reaction. All values of T were of course obtained indirectly by subtraction of the quantities of barium hydroxide from the fifteen cubic centimeters of acid employed. V is the volume of the pipette, and N the normality of the hydrochloric acid in terms of which the reaction was measured.

In the tables are given the values of K and of the periods in minutes over which the reactions proceeded with measurable velocity.

TABLE I.

Reaction at 0°.

Ester	Ethyl acetate	Ethyl glycollate	Ethyl methyloxy acetate	Ethyl ethyloxy acetate	Ethyl propyloxy acetate
Time	300	35	25	25	25
K	1·24	13·8	36·7	13·8	12·6
	1·21	13·5	39·5	18·6	12·8
	1·20	(9·7)	40·3	16·8	13·8
	1·14	12·3	37·7	15·8	12·9
	1·13	12·6	36·4	14·5	13·0
	1·11	12·4	33·7	15·4	11·4
	1·16	---	30·5	---	12·3
Averages	1·17	12·9	36·4	15·9	12·7
Averages (duplicate)	1·19	12·8	37·1	15·2	12·9

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* Findlay, Practical Physical Chemistry, p. 243. Ostwald-Luther, loc. cit.

TABLE I (continued).

Reaction at 25°.

Ester	Ethyl acetate	Ethyl glycollate	Ethyl methyloxy acetate	Ethyl ethyloxy acetate	Ethyl propyloxy acetate
Time	60	10	5	15	12
K	6·60	(56·4)	156·	66·4	52·8
	6·60	65·7	146·	62·4	(59·8)
	6·85	67·6	119·	62·4	51·7
	6·63	61·7	117·	62·3	52·8
	5·89	68·6	104·	70·2	51·3
	6·78	63·0	---	65·3	---
Averages	6·56	65·3	128·	64·8	52·1
Averages (duplicate)	6·54	65·3	118·	61·8	49·1

TABLE II.

Reaction at 0°.

Ester	Ethyl propionate	Ethyl lactate	Ethyl glycerate	Ethyl α ethyloxy propionate	Ethyl β ethyloxy propionate
Time	275	25	25	180	185
K	1·24	14·4	9·40	2·57	1·15
	1·15	15·3	9·80	2·09	1·15
	1·12	14·5	9·20	2·09	1·13
	1·20	13·8	8·70	1·98	0·98
	1·11	14·4	8·88	1·89	1·00
	1·05	14·6	8·15	1·81	1·02
Averages	1·14	14·6	9·02	2·07	1·07
Averages (duplicate)	1·18	14·3	11·2	1·92	1·10

Reaction at 25°.

Time	90	10	10	110	80
K	5·82	63·9	52·6	9·52	5·63
	5·88	64·1	53·2	9·12	5·28
	6·17	63·8	57·2	8·76	5·20
	6·31	68·3	55·3	9·06	4·93
	6·13	62·5	57·8	10·0	5·14
	5·73	59·7	60·1	---	5·02
	5·88	---	64·6	---	4·46
Averages	5·94	63·7	57·3	9·29	5·02
Averages (duplicate)	6·16	64·6	59·4	9·33	4·87

TABLE III.—Summary.

A

Ester	K(0°)	K(25°)	k(aff)*
Ethyl acetate	1·17	6·56	·0018
Ethyl glycollate	12·9	65·3	·0152
Ethyl methyloxy acetate	36·4	128·	·0335
Ethyl ethyloxy acetate	15·9	64·8	·0234
Ethyl propyloxy acetate	12·7	52·1	----
Ethyl propionate	1·14	5·94	·00134
Ethyl lactate	14·6	63·7	·0138
Ethyl glycerate	9·02	57·3	·0228
Ethyl alpha-ethyloxy propionate	2·07	9·29	----
Ethyl beta-ethyloxy propionate	1·07	5·02	----

B

Ester	K(25°)	k(aff)*
Ethyl acetate	6·5	·0018
Ethyl glycollate	75·	·0152
Ethyl propionate	5·3	·00134
Ethyl lactate	63·5	·0138
Ethyl phenylacetate	12·4	·0056
Ethyl mandelate	66·	·0417
Ethyl methyloxy phenylacetate	23·	·074
Ethyl ethyloxy phenylacetate	15·7	·053
Ethyl propyloxy phenylacetate	13·3	·049

Discussion of Results.

In the first part of the summary table are given the averages of the series printed in full in Tables I and II. In addition are stated the dissociation constants of some of the acids as determined by Ostwald. The second part of the table contains results taken from the paper of Findlay and Hickmans,[†] which seem to be of interest in relation to our work. The figures in two cases do not agree, and this discrepancy is deserving of slight discussion. Our constants for ethyl glycollate saponified at twenty-five degrees are much lower than those of Findlay. After a study of the possibilities of error in our method we are of the opinion that Findlay's results, obtained by the conductivity method, may be the more accurate. We have not, however, been able to duplicate his results. In the other case, that of ethyl propionate, we are convinced that Findlay's figure is decidedly too low. Calculations from the results of Reicher,[‡] obtained at a lower temperature, indicate a value of 5·7 +. Our value of 5·9 is nearer than that of Findlay, which is 5·3. In addition we would say that it is probable that the figures for

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[*] Ostwald, Zeitschr. phys. Chem., iii, 176. Findlay and Turner, Jour. Chem. Soc., xcv.

[†] Loc. cit.

[‡] Loc. cit.

some of the other esters in our list are probably too low for the work at twenty-five degrees. The ratios obtained from the constants for zero degrees have been considered of more weight in the study of the results.

After a fairly close examination of the above figures we have been unsuccessful in an attempt to obtain conclusions of very general value. The one thing most apparent is that the velocity of saponification of the ester is closely connected with the strength of the acid from which it is derived. This is in accord with the theory set forth by both Hjelt* and Sudborough,† that the velocity of saponification is controlled by two factors, the strength of the acid and steric influences in the molecule. At present we are unable to obtain any mathematical expression which will be of value in predicting the magnitude or direction of these steric influences.

Two or three points brought out by the tables deserve mention. The effect of alkyloxy groups is very varied. Extreme cases are those of the esters of methyloxy acetic and beta ethyloxy propionic acids, which have respectively the greatest and least velocities of all the series. The effect of the hydroxyl group is nearly the same in the cases of glycollate and lactate, but is decidedly less in the case of ethyl mandelate. In ethyl glycerate steric influences prevent any logical comparison. Finally it is to be noted that the ratios of saponification of these esters are entirely different from those of their velocity of hydrolysis in acid solution.

Summary.

1. The presence of a hydroxyl group in aliphatic esters seems to produce an acceleration in the velocity of saponification, although this effect is variable in its magnitude.

2. (a) Alkyloxy groups may cause an effect varying from a tremendous acceleration to a slight retardation in different cases.

(b) The velocity of saponification of alkyloxy esters of similar constitution decreases with the size of the substituted group.

3. Beta substituted esters seem to decompose less rapidly than isomeric alpha products, a single point of resemblance to effects produced in acid hydrolysis.

4. The velocity of saponification is very largely controlled by the strength of the acid from which the ester is derived.

It is our intention to continue this study on the velocities of several other esters and obtain if possible data which will enable us to draw more general conclusions on the subject.

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* Loc. cit.

† Proc. Chem. Soc., xiii, 241.

ART. LII.—*Some Kilauean Ejectamenta*; by FRANK A. PERRET.

IMPRESSED by all that has been said as to the essentially quiet nature of Kilauean volcanism in modern times, the observant visitor experiences a mild surprise at finding on all sides the most conclusive evidence of explosive action, of which some of the products, by their superposition and freshness of aspect, can with difficulty be relegated to the time of the last recorded great explosive eruption in 1790.*

FIG. 1.

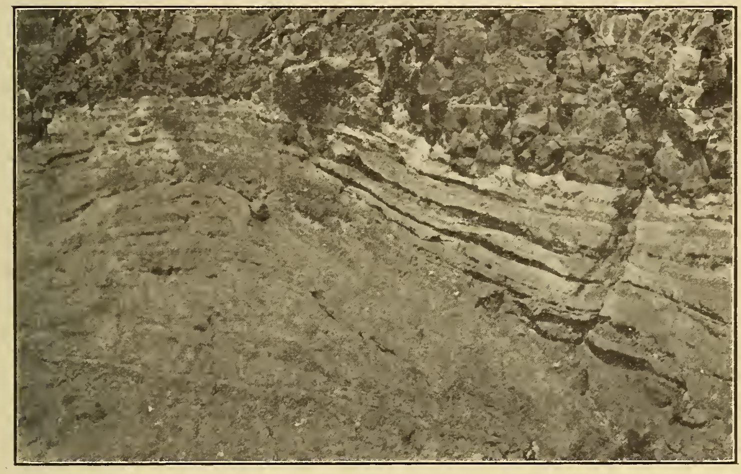

FIG. 1. Kilauea. Main crater. Detail of west wall showing ash and lava strata.

The walls of the great pit-crater, in whose exposed strata the investigator may read the story of the long ago, show in most places, it is true, a continuous series of overlying lava flows, but at other points—in the azimuth planes of the principal winds—the series of rock layers is interrupted by imposing beds of ash (fig. 1), while in regions of more recent activity, within the greater pit, erosion has revealed a depth of many

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* Some say 1789. Several explosive phases occurred during the nineteenth century. The absence of reliable information as to these products makes one more than ever regret the days—now happily past but still all too recent—when regular, systematic observation was not carried on at this volcano.

meters in those ash beds which, from their elevated positions, have escaped interment by subsequent overflows of lava from Halemaumau.

Imbedded in this ash are to be found innumerable "pisolites" (fig. 2), which, being of aërial formation, speak even more eloquently of an ash-laden atmosphere than do the massive beds —especially to one who has experienced the conditions of their formation. These Kilauean pisolites are large, often exceeding the size of a pea (*), and, while the majority conserve their original freshness and fragility, a few of the more exposed have become so indurated as to be handled roughly without fear of collapse.

Fig. 2.

Fig. 2. Kilauea pisolites, free and imbedded in massive ash.

Scattered about upon these fields of ash, and even to a considerable distance from the craters, Halemaumau, Kilauea-iki and Keanakakoi, one may see a great quantity of angular blocks of lava rock, ejected in that condition, and also many true

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[*] At Vesuvius, in 1906, the fully formed pisolites which retained their shape in falling were generally much smaller, but the writer was frequently pelted with balls of *liquid* mud larger than a walnut.

bombs of lava which was liquid at the moment of expulsion. Some of the latter are homogeneously solid; others have a nucleus of more vesicular lava covered with a compact shell, while all show a lesser tendency to form tail-like extensions at the extremities than those of Etna and Vesuvius. This is explained by the lesser viscosity of the Hawaiian lava permitting of a spherical adjustment during trajectory which, however, is generally modified by the revolution of the mass and results in a figure which is nearly elliptical (fig. 3). This

Fig. 3.

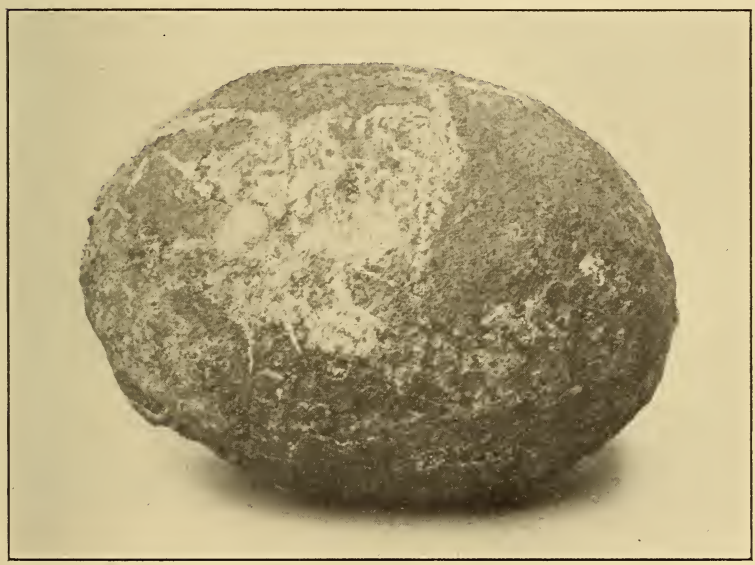

Fig. 3. Elliptical bomb from Kilauea.

bomb has a length of 10^{cm} and weighs 660 grams, the nucleus being somewhat scoriaceous with an exceedingly compact shell of 1^{cm} in depth.

A very small, compact bomb found by the writer compares with the similar ones from the 1909 eruption at Teneriffe and from Vesuvius and Etna, as follows:

	Wt.	Sp. Gr.
Kilauea	25·51 g.	2·89
Teneriffe	25·52 "	2·92
Vesuvius	13·50 "	2·50
Etna	16·61 "	2·15

Those of Vesuvius and Etna are slightly scoriaceous, which accounts for their lower specific gravity. These products of Pacific, Atlantic, and Mediterranean volcanoes are so similar in size, form, and general appearance as to require marking for identification.

At Kilauea the ejection of these bombs and blocks took place after that of the ash, in which they are imbedded to the extent of about one-half of their mass. The bombs have been slightly deformed by the impact, which has produced, on the surface of the ash field, a circular, depressed area, resembling a fish's nest, in the center of which projects the comb or block, as shown in fig. 4.

Fig. 4.

Fig. 4. Showing effect upon sand produced by impact of falling block or bomb.

In a region exposed to strong wind and torrential rains it is difficult to believe that such formations could withstand a century of weathering. At Stromboli, in 1912, precisely similar impact depressions were obliterated by the first heavy rain, but in this case the ash, newly fallen, had not become compacted, and here we have an additional reason for believing the formation of the Kilauean ash beds to have considerably preceded the ejection of the solid blocks and bombs.

The largest of the true lava bombs found by the writer at Kilauea is shown in fig. 5. It is of the turtle-back variety, of a more viscous lava than the preceding, and is now in the Bishop Museum at Honolulu.

Of greater interest from the standpoint of novelty are the miniature bombs or lava drops represented in fig. 6. These were discovered by the writer on the top, and surrounding the base, of several small, dome-topped cones of very scoriaceous lava situated on the northern rim of Kilauea near "Kaniakolea," and therefore *outside* of the great pit crater, although within one of the surrounding areas of subsidence and not very far from the "Sulphur Banks," which are in the active solfatara stage of volcanism.

Fig. 5.

Fig. 5. Large turtle-back bomb. Kilauea.

The tiny bombs were evidently blown through the open channels in the scoriaceous lava of the cones, which acted as a sieve in subdividing the liquid into drops, these taking various stages during trajectory according to their manner of projection. The filamentary ejecta of fountain action being quite generally known as "Pele's Hair," these curious little formations might be termed "Lacrimæ Pele"—"Pele's Tears"—many having the exact shape of a tear-drop. The form which is most prevalent is that of a dumb-bell, which is especially interesting as showing the effect of longitudinal rotation during trajectory in sending the greater mass of the liquid to the ends by centrifugal force.

The material is a greenish glass, indicative of the rapid cooling, and which is highly vesicular—more than one-half of the mass consisting of gas vesicles. Notwithstanding this fact, the surface skin is uniformly continuous, giving no indication of the interior condition, and is of a matte-smooth finish almost black in color. The presence of gas vesicles in the interior lowers the specific gravity of the drops, as units, to an average of about 1·04, some of the larger specimens having less than 1·00 and floating in water.

Fig. 6.

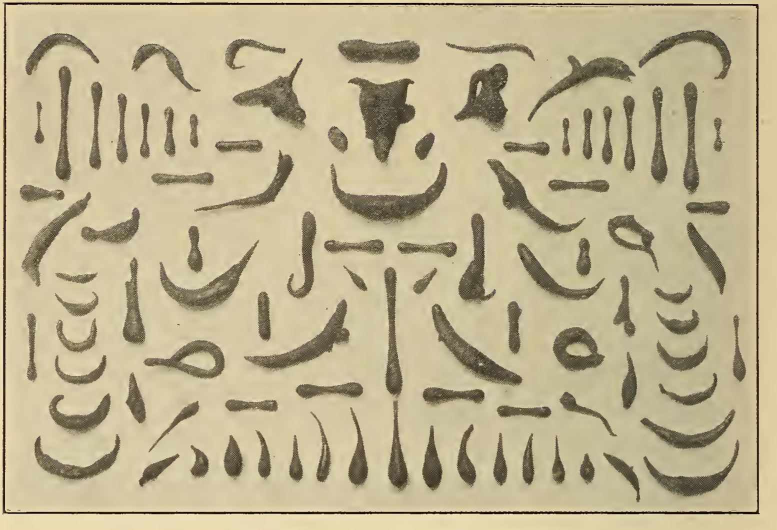

Fig. 6. Miniature bombs or lava drops.

It would be interesting to know if these drops are due to fresh lava welling up through the cones of ejection, or whether—as suggested to the writer by Mr. I. Friedlaender—they may be a refusion product of the substance of the cones. It is hoped that this and other points may be determined by a microscopic and chemical analysis. In the lightness and fragility of the product, together with the unaltered surfaces, we have reasons for supposing the formation to have been comparatively recent.

As is so frequently the case, when a new product is discovered in one locality it is afterwards found in many places ;

and guests of the Volcano House, on seeing these drops, soon picked up others beside the trail leading down into the crater, while, by a curious coincidence, an assistant of Professor Brigham, in ascending Hualalai, found a number of similar ejections, but which are of a larger and coarser habit of formation. It seems probable, therefore, that their production is quite common to volcanoes of this type and that it is the result of a secondary phase of activity in localities of comparatively recent eruption.

Fig. 7.

Fig. 7. Fine and coarse lava filaments. (Pele's Hair.)

The most common and the most continuously formed of all Kilauean ejecta are the vitreous filaments, commonly called Pele's Hair—so well known and so frequently described as to render superfluous a detailed consideration here. Very fine and very coarse specimens are together reproduced in fig. 7, the straight, thick wire having been found by Miss Thurston, and kindly presented to the writer. The sponge lava or "thread lace scoria" has also been fully described,* and, furthermore, all of this material observed by the writer lay upon the pahoehoe lava in a continuous stratum, indicating formation *in situ* and therefore not to be included under the head of ejectamenta.

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* Dana, "Characteristics of Volcanoes."

Returning now for a moment to our first proposition, we find in Kilauea a volcano whose past activity has been characterized by the ejection of large quantities of ash as well as by the emission of lava, and yet whose form is that of the flat dome with gentle declivities so characteristic of the Hawaiian type. It is obvious that, although ejected ash may often accumulate to a somewhat greater depth in the immediate neighborhood of the vent, especially if coarser particles are present, yet, on the whole, its manner of coming to earth is in the nature of a sedimentary deposit, taking and maintaining the general form of the surface upon which it falls. We may venture, then, to enunciate the principle that *the ejection of ash need not, per se, materially affect the form of the volcanic edifice*, that being the function of the degree of viscosity of the fluent lava and of the presence of larger fragmentary ejecta. We should not conclude, therefore, that a flat dome is necessarily composed entirely of massive lava and that its past activity has been free from the explosive emission of ash.

In regions where civilization is recent and true history does not extend far into the past, the native tradition becomes of enormous importance, especially when it can be compared with, and controlled by, the local geological revelations. That relating to Kilauea is rendered by the Rev. W. D. Westervelt as follows:

Tradition—Kirauea.

"In earlier ages it used to boil up, overflow its banks and inundate the adjacent country; but for many king's reigns past it had kept below the level of the surrounding plain, continually extending its surface and increasing in depth and occasionally throwing up with violent explosions huge rocks or red-hot stones. These eruptions were always accompanied by dreadful earthquakes, loud claps of thunder and vivid and quick succeeding lightning. No great explosion had taken place since the days of Keoua (1790) but many places near the sea had since been overflowed, on which occasions Pele went by a road underground from her house in the crater to the shore. Kirauea had been burning ever since the islands emerged from night. 'Mai ka po mai'—from chaos until now."

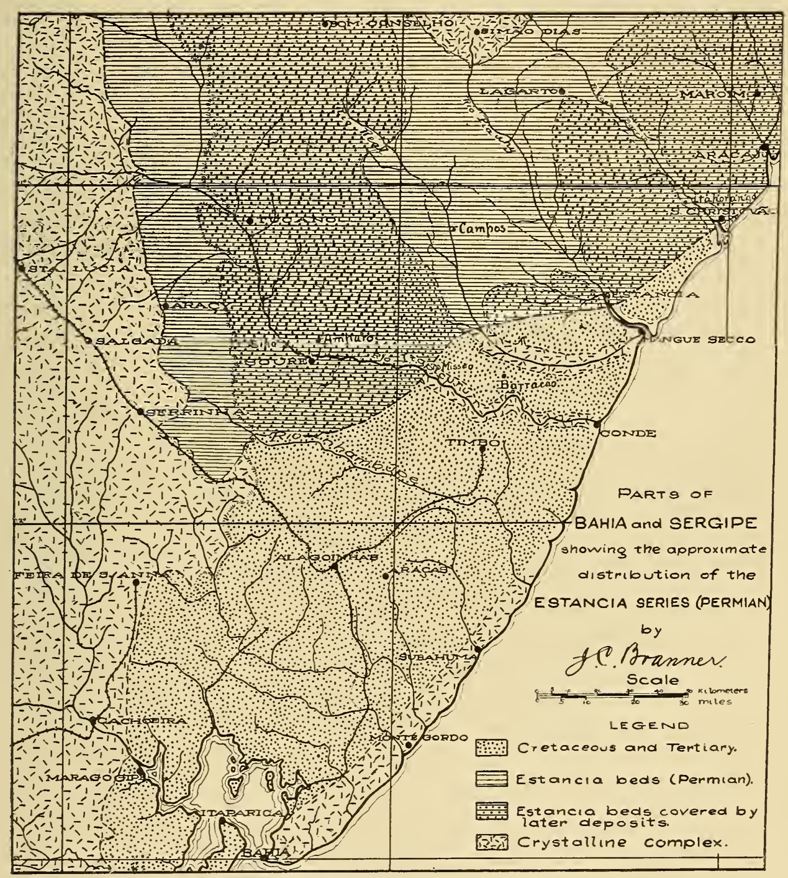
In this picturesque little tradition we have the story of the volcano—the formation of the dome by centrifugal overflows from a central vent; the period of subsidence with the formation of a great pit or caldera; the explosive phases with volcanic lightnings testifying to great quantities of ash; the subsequent lateral subterranean outflows of lava to the sea—a volume could be devoted to its expansion.

April 2, 1913.

ART. LIII.—*The Estancia Beds of Bahia, Sergipe, and Alagoas, Brazil*; by J. C. BRANNER.

THE existence of recognizable fossil plants in the Estancia beds of Brazil was first discovered in digging a well on fazenda Jacú, about six and a half kilometers northeast of the village of Aracy, formerly known as Raso, in the state of Bahia. This discovery was made in 1910 when specimens of the fossils were sent to O. A. Derby, chief of the Geological Service of Brazil at Rio de Janeiro. Mr. Derby wrote me about the matter, and

FIG. 1.



in June, 1911, while on a visit to the interior of Bahia, I made a point of visiting the locality for the purpose of making sure of the stratigraphy of the surrounding region in relation to the fossil-bearing beds.

The accompanying sketch-map, made up partly from the Serviço Geologico's map of Bahia by Branner, Crandall, and Williams, and partly from later personal observations, will give some idea of the general geography and geology of the place and of its relations to the coast geology.

Fig. 2.

Fig. 2. Section at Riacho da Cruz six kilometers south to Aracy where the Estancia beds rest against the granites.

In order to reach Aracy I left the railway at Serrinha, a station on the Bahia and S. Francisco railway. Salgada, another railway station north of Serrinha, is somewhat nearer Aracy, but the facilities for getting horses there for the trip across country are not so good.

Fig. 3.

Fig. 3. East-west section showing the general geology across the western edge of the Estancia beds south of Aracy.

Aracy is about thirty-eight kilometers north of Serrinha. The road from Serrinha passes at first over the granites, gneisses, and crystalline schists that make up the Archean complex over most of the northeastern part of Brazil.

Ten kilometers north of Serrinha I found many water-worn fragments of flint scattered over the surface of the ground. These fragments continue along the road northward and become more abundant as the area of sedimentary rocks is approached. They rest on the eroded surfaces of the decomposed crystalline rocks.

At and about the village of Pedras, twenty kilometers north of Serrinha, granites are well exposed. North of Pedras the road descends a granite hill near the base of which sandstones rest against the granites. This is the Riacho do Massapé Bonito or Riacho da Cruz shown in figure 2. The hill to the north is about 15 meters high, and the granite hill to the south extends to and south of the village of Pedras. From this contact northward to Aracy the road passes over a series of horizontal red, brown, and yellow sediments that form a plateau shouldering up against hills of granites and schists on the west.

Looking eastward from this place one sees a flat sky-line, while the intervening plain is dotted here and there by outlying peaks and small mountains that were found to be of granite in some cases, and in others remnants of the sedimentary beds.

FIG. 4.

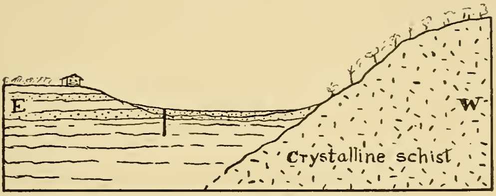


FIG. 4. Section at Serra Azul where the Estancia beds rest against crystalline schists.

These sedimentary beds are mostly false-bedded sandstones of a dark chocolate color. They and the accompanying shales were hastily examined for fossils, but, with the exception of a few bits of unrecognizable wood, none were found.

At a place called Serra Azul, about three kilometers south of Aracy, a well was being bored by the federal bureau "Inspectoria de Obras contra as Seccas." The geology of the place about the well is simple. The well is being sunk in the sedimentary beds that rest unconformably against crystalline schists that are exposed in the hills not more than 150 meters southwest of the well. At the time of my visit, June 21, 1911, the well had passed through three meters of sand and one meter of sandrock in place.

The horizontal Estancia beds continue to within one kilometer of Aracy. Here is an outcrop of pink granite just west of the road, but evidently very close to the edge of the sedimentary series which underlies the village of Aracy itself.

The village of Aracy stands upon the Estancia sandstones, and a well has been drilled in the public square.

LOG OF THE WELL OF ARACY.

Clay and soil	4·7	meters
Sandstone	18·	"
Red clay	20·	"
Sandstone	4·	"
Total	56·7	meters

In the hills three kilometers north of Aracy on the Tucano road are exposed red clays with greenish streaks and splotches at the base. The clays are twenty-five meters or more in thickness and rest upon the sandstone that underlies the town of Aracy. They are followed higher up by an outcrop of granite, but still farther north the red false-bedded sandstones appear again, dipping 11° N. 50° W. magnetic.

Fig. 5.

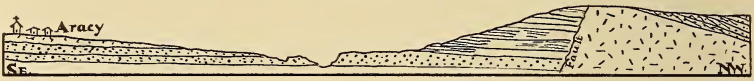


Fig. 5. Section about three kilometers long northwest from Aracy, showing the faulted Estancia beds against granites.

The exposures of sandstone at this place are more than sixty meters across. The rocks have a rusty color on the outside, and are of a buff color on the inside. Usually the surfaces of these exposures are covered with a thin black coating of manganese.

Col. Larangeiras of Aracy, who is remarkably well acquainted with the geology of the surrounding region, informs me that the ridges west of the town are all of granitic rocks, but that the region to the east of these ridges is all of the sedimentary beds as far as Soure. He notes also that the sedimentary beds are not confined to the table lands on the east, but that everywhere they extend far west of the table lands.

Fig. 6.

Fig. 6. Section across the western edge of the Estancia series near Aracy.

Fazenda Jacú, where the fossil plants have been found, is six and a half kilometers northeast of Aracy. The place belongs to Francisco Ferreira da Motta, the son of Col. Larangeiras, who was most cordial and helpful in giving information and aid. The road from Aracy to Jacú passes all the way over loose yellowish red sand with here and there loose fragments of the Estancia sandstone which appears to underlie the region.

The section given here shows the relations of the fossil-bearing shales to the sandstone of Jacú, as indicated by the natural exposures and in a well put down at that place.

FIG. 7.

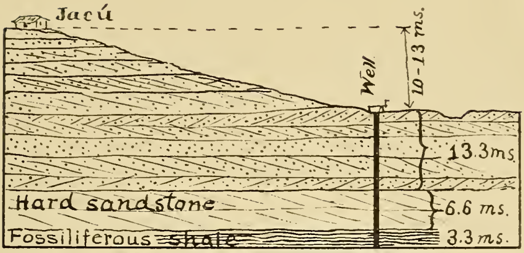


FIG. 7. Section showing the relations of the red sandstones to the fossil-bearing shales in the well at fazenda Jacú.

The section passed through in the Jacú well, as furnished me by Col. Larangeiras and his son Francisco Ferreira da Motta, is as follows:

LOG OF THE WELL AT JACÚ.

Rock	Depth	
Reddish soft sandstone	13·3	meters
Somewhat harder sandstone	6·6	"
Dark lead-colored shales, with plant impressions	3·3	"
	23·2	meters

There were no facilities for getting down in the well at the time of my visit, but from what I could see from the surface and from the character of the material on the waste heap and the fossils found in the shales, the record must be practically as represented.

In the natural exposures the sandstones dip gently toward the east, and in the well itself the beds are so nearly horizontal that no dip is apparent. Col. Larangeiras says the sandstones exposed hereabout continue as far as the plateau, some thirteen to sixteen kilometers to the east, while my knowledge of the geology of the plateau region leads me to infer that these Estancia beds pass beneath the tablelands.

The fossils found in the well at Jacú consist of the impressions of ferns and occasional fragments of carbonized wood and of silicified wood, all of which are scattered through the shales. The fossil ferns are described by David White in the accompanying paper.

The section and profile herewith will give an idea of the geology of the region along the road leading southward from Aracy to Serrinha. (See fig. 9.)

Inasmuch as Dr. White's determination of the Permian age of these beds is the first one to place them in the geological series by means of fossils, it seems worth while to give, in connection with these local notes, such information as I have in regard to the distribution of the Estancia series in Bahia, Sergipe and Alagoas.

It should be kept in mind, in regard to these notes, that there has not been found as yet any paleontologic evidence of the identity of the beds here spoken of as Estancia beds, and that Jacú is the only place where recognizable fossils have been found. However, the lithologic characters of the series and their relations to other rocks are so constant that there seems to be but little chance of being mistaken about the identity.

Fig. 8.

Fig. 8. The Estancia red sandstones at fazenda Jacú near Aracy.

Distribution of the Estancia beds in the State of Bahia.—The approximate area of the Estancia beds in eastern Bahia and Sergipe is shown on the accompanying sketch map (fig. 1). For lack of better maps a more detailed distribution cannot be given at present. It will be seen that the beds extend from the neighborhood of Aracy northward and southward along the westward flank of the Cretaceous-Tertiary table lands. I am not at all sure about how far northward they extend. To the south they have not been certainly recognized as crossing the line of the railway between Serrinha and Alagoinhas, though it is quite possible that they do cross it south of kilometer 103 and between 89 and 91, and at many places south of kilometer 84. But inasmuch as the later plateau beds end just east of Agua Fria, and as the Estancia beds do not appear on Rio Itapicurú just north of Timbó, or on Rio Real north of Barracão, it seems evident that they lie in a basin that extends eastward from Aracy to and beyond Estancia. The southern edge of this basin is overlapped by later deposits, but it seems to be close to a line drawn between Serrinha and Estancia.

Fig. 9.

Fig. 9. North-south section from the village of Pedras to Aracy showing the Estancia beds overlying granites.

In June, 1907, I made a trip from Bahia to Rio Itapicurú north of Timbó, expecting to find these Estancia rocks exposed along that stream. The Itapicurú at Engenho Brauna, on the road between Timbó and Barracão, was found to run over granites and crystalline schists, while the overlying sedimentary beds forming the plains are Cretaceous or Tertiary. Evidently then the seaward margin of the Estancia beds swings inland south of Estancia and does not appear beneath the Cretaceous beds on Rio Itapicurú where that stream is crossed by the Timbó-Barracão road.

Fig. 10.

Fig. 10. North-south section across Rio Itapicurú at Engenho Brauna, 12 kilometers north of Timbó, State of Bahia. Mesozoic sediments forming the plateau rest upon granites, gneisses, and schists.

Reports regarding the character of the rocks in the vicinity of Patamuté in the northeastern part of the state of Bahia lead me to suppose that the Estancia beds occur in that part of the state.

Beds that appear to belong to the Estancia series have been seen by me at many places west of the railway running from Bahia to Joazeiro.

West of Campo Formoso on the watershed between Rio Itapicurú and Rio Salitre drainage I found at several places a basal conglomerate and reddish sandstone that closely resemble the Estancia beds. They rest upon reddish granites and dip westward beneath the Salitre valley. They are overlain by gray thin-bedded limestones.

No fossils were found in either the sandstones or the limestones though diligent search was made. This section was the first to bring out clearly the relation of limestones of the Salitre valley to the Estancia beds.

Descending from the watershed into the Salitre valley at Varzinha one finds red shales interbedded with the dove-colored limestones. West of the Salitre valley on fazenda Ingazeira I found red sandstones near the base of the Serra do Angico.

One and a half kilometers east of the village of Lage where the Riacho do Inferno or Rio Escurial issues from the mountains there is a hill of gray thin-bedded limestone 232 meters high on the south side of the valley that forms the north end of the Serra do Angico. This limestone seems to rest unconformably against the sandstones and quartzites of the Serra do Angico and to have sandstones beneath it—probably the Estancia beds. Similar limestones form the hills five kilometers west of Lage on both sides of the Rio Escurial.

Fig. 11.

Fig. 11. General east-west section across Serra de Jacobina through Campo Formoso. The Estancia beds are on the Salitre Valley side and small patches appear on the east side of the watershed.

Through the region northwest of Lage and as far as the Rio São Francisco no beds were seen that could be identified as belonging to the Estancia series. In the Calmon valley, however, are limestones and red sandstones that possibly belong here.

About the head waters of Rio Salitre and lying between Almas valley and Morro do Chapeo is a great uninhabited catinga plain bounded by the Serra de S. Mauricio on the east and by the mountains at Gruna and the Serra do Bautista on the west. Around the margins of this plain appear at many places limestones overlying sandstones that seem to belong to the Estancia series. These rocks rest unconformably upon the sandstones and quartzites of the Lavras (Carboniferous ?) series and against the older Caboclo (Devonian ?) shales.

Some twenty kilometers south of the village of Alagoinhas the red sandstones and limestones are exposed on the trail leading to Gruna. Similar sandstones and limestones were seen near Rodelleiro and in the vicinity of the village of Gruna.

Crossing the mountains (Serra do Bautista) southwest of Gruna one comes out upon a great flat plateau that is deeply cut by the main stream, that is by the Rio Jacaré, and by its tributaries, and above which rise here and there isolated peaks and small mountain clusters. Following the trail from Riacho Feio past the villages of Jacaré, Chapada, and Carahyba to America Dourada, limestone is the principal rock to be seen everywhere. The beds are generally closely folded, and even stand on end over large areas. Fossils were diligently looked for but the only ones found were oölites apparently deposited by marine algæ.*

On the road from America Dourada to Morro do Chapeo one gets a good idea of the relations of the limestones to the diamond-bearing Lavras beds that form such a large part of the geology about and south of Morro do Chapeo. The section where the serra merges into the plateau to the west is here generalized.

FIG. 12.

FIG. 12. General east-west section from the plains near America Dourada to near Morro do Chapeo.

The Estancia red beds are not known in the immediate vicinity of Morro do Chapeo, but south of there about forty kilometers they are exposed on the upper part of Rio Salitre at a camping place on fazenda Gaspar and along the east side of that stream to the village of Tabúa, a distance of twenty kilometers. At and south of Gaspar the lowest rocks exposed are quartzites that appear well exposed in the stream bed of Rio Salitre. About 300 meters north of the camp, and apparently resting on the quartzite is a red shaly sandstone overlain by a basal conglomerate made up partly of arkose and partly of waterworn blocks of a reddish crystalline rock from one decimeter to half a meter or more in diameter and of blocks of quartzite. The quartzites contain small granite bowlders.

Farther down stream (Rio Salitre) hills of pink marble follow the direction of the road leading to Tabúa. Beneath the marble or other limestone beds red sandstone or conglomerate occasionally crops out. The conglomerate contains both angular and waterworn fragments of crystalline rocks, some of which are reddish granites. No fossils could be found in any of these rocks.

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* Bull. Geol. Soc. America, xxii, 189–191.

Going south from Morro do Chapeo, by the road leading to Lençoes by way of Antonio José, Riachão de Utinga, Bello Horizonte and Pegas, one passes over rocks of the Lavras series and over the Caboclo shales until he reaches the vicinity of fazenda Mulungu where the Rio Utinga and Rio do Burity unite. From there southward appear signs of the Estancia red sandstones and shales and their accompanying limestones. On fazenda Bello Horizonte slabs of shaly limestones are exposed where the road crosses the bridge over Rio de Lages. At Ponte Nova on Rio Utinga there is an exposure of red shale on the right bank of the river about twelve meters above the bridge.

The beds are nearly horizontal; the rock is of a dark purplish red and has light leached spots through it. It is just like the red shales seen beneath the limestones at other places. No signs of fossils were found in the shale at Ponte Nova.

Fig. 13.

Fig. 13. Section showing the structure at Mocambo.

Mr. Waddell of Ponte Nova tells me that limestone outcrops two kilometers east of Rio Utinga, and that it continues for about twenty-five kilometers farther to the east where the road passes onto the granitic rocks of central Bahia. Between Pegas and Rio Bonito the road passes onto the Lavras beds. Traveling southward by way of Lençoes and Andarahy one sees no more of the Estancia series until after Rio Paragurassú is crossed at Bichinho. Near Lagoa do Leite red shales appear by the roadside. West of the lake is a hill that seems to be made of the red shales capped with limestone.

The general geology at the village of Mocambo is shown in the accompanying section.

A bluish conglomerate bed exposed at and about Mocambo contains waterworn pebbles of the Lavras pink quartzite, and also pebbles of basic eruptive rocks. Overlying the conglomerate is a series of red shales such as are sometimes found in the Estancia series.

Following the road southeast from Mocambo toward Bandeira de Mello loose flints are abundant, apparently weathered out of the limestones above the red shales. At and about

Macaco Secco limestones and red shales are exposed. At Rio Una the limestone is exposed in bluffs 30 meters high in nearly horizontal beds.

Descending the steep hill at Canna Brava close to Rio Paraguassú blocks of the red Estancia sandstones and a few pieces of limestone strew the slopes near the road. On the flat ground at the base of the hill and close to the river light pinkish limestone is exposed in place.

At and about the inn at Tamanduá the Estancia red sandstone is exposed. Three hundred meters downstream from the inn great ledges of it are well exposed on the south side of the Rio Paraguassú. The beds here are jointed, and consist of both sandstone and conglomerates. Three hundred meters up stream from the inn granite blocks fill the channel of the river. Two and a half kilometers north of the village of Bebedouro coarse red basal conglomerate is exposed. One kilometer or less north of Bebedouro the Estancia beds outcrop at the base of the mountain, red granite is exposed at the southern edge of that village, while just west of it, at the base of the ridge, the Estancia beds crop out in long horizontal ledges and in blocks.

Evidently the Estancia beds on this part of the Paraguassú rest directly upon the granites and attain a thickness of more than a hundred meters. From this place to the railway at Bandeira de Mello and thence to Caxoeira on the bay of Bahia the rocks are all granites, gneisses, and other old crystalline rocks. The zone of Estancia beds has a width of fifty kilometers where they are cut through by the Rio Paraguassú between Bebedouro and Bichinha near Andarahy.

The Estancia beds in the state of Sergipe.—The first brief description of the red sandstones found at the town of Estancia in the state of Sergipe, was published in 1870 in Hartt's Geology and Physical Geography of Brazil at page 379. Hartt says of them: "Estancia is built on a rolling country, where the heights of the immediate vicinity are not more than two or three hundred feet. The hills are rounded, and the rocks comprising them are coarse red micaceous sandstones, quite indistinguishable in the hand specimen from the Triassic red sandstone of New Jersey. This sandstone covers a large area, and must be very thick. I examined it in several places, but found no signs of fossils. The dip, as a general thing, appears to be a few degrees to the eastward."

In 1875, during the existence of the Commissão Geologica and as one of the geological assistants, I worked on the geology of Sergipe, visited Estancia, and crossed the region between that place and the base of the Serra de Itabaiana for the purpose of determining the relations of the Estancia beds to the mountains of the interior. It was found that the Estancia beds were overlapped by fossiliferous Cretaceous beds on the southwest, while to the west they rest upon an older series of sediments, sandstones, and shales probably Carboniferous and Devonian, that form the crest and southern flank of the Serra de Itabaiana. At the time limestones were found near the Estancia red beds east of the Serra de Itabaiana and above the red beds at Itaporanga, but it was not then clear that the limestones were part of the Estancia series. No fossils have yet been found either in the sandstones or the limestones of the Estancia series in Sergipe.

FIG. 14.

FIG. 14. The Estancia red sandstones exposed in the bed of Rio Piauhy at Estancia, Brazil.

Northeast of Estancia the red sandstones were found at and about Itaporanga, and at São Christovão. East of the latter place they have not been found in the state of Sergipe.

In 1907 I sent an assistant, Roderic Crandall, into the region north of Timbó and he reported that the Estancia red beds appear on the Rio Real some fifty to sixty kilometers north of Timbó and that they extend up-stream some fifteen kilometers above the village of Campos and eastward to Rio Piauhy, crossing that stream at Lagoa Vermelha. From this point they form a narrow belt that extends northward to Lagarto and thence follow down Rio Vasa Barris. He found the western margin of this area in the state of Bahia about thirty-five kilometers southeast of Bom Conselho. The structure as given in one of Mr. Crandall's letters is shown in figs. 15 and 16.

The Estancia beds in Alagoas.—The occurrence of the beds of the Estancia series in Alagoas was first noted by the English botanist, George Gardner, who visited Penedo in 1838. He states that the rock on which that city stands is a fine-grained yellowish sandstone.*

Professor Hartt, in his Geology and Physical Geography of Brazil, also speaks of the Penedo sandstones, but he did not correlate them with the Estancia beds. The writer visited Penedo in 1875 and found in the lower parts of the series, just north of the ledge on which Penedo stands, fragments of fossil plants. When the Commissão Geologica was abolished by the government these fossils were turned over to the National Museum in Rio de Janeiro, but nothing has ever been done with them. They were very poor, however, and mostly unrecognizable. The sandstone beds dip toward the southeast, and strike into the interior of the state of Alagoas. On later trips made across the state of Alagoas along the railway the Estancia beds were not found,† and it is therefore inferred that they are concealed by the Tertiary beds in the eastern part of Alagoas, and that they thin out toward the east and do not reach the state of Pernambuco near the coast. The hypothetical distribution of the Estancia beds in Alagoas is shown on a map published by the writer in 1910.‡

FIG. 15.

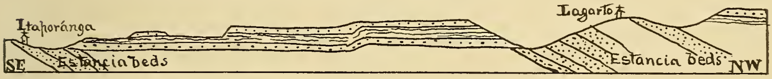

FIG. 15. Section from Itaporanga to Lagarto, by R. Crandall.

FIG. 16.

FIG. 16. Section from Estancia to Itaporanga showing the Tertiary resting on the Estancia beds, by R. Crandall.

Conclusions in regard to the Estancia Series of Brazil.—The Estancia series of Brazil, named for the town of Estancia

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*George Gardner: Travels in the interior of Brazil. 2d ed., London, 1849, p. 88.

†J. C. Branner: Two characteristic geologic sections on the northeast coast of Brazil, Proc. Wash. Acad. Sci., II, 185–201, Washington, 1900.

‡J. C. Branner: The geology of the coast of the state of Alagoas, Ann. Carnegie Museum, VII, 5–22, Pittsburg, 1910.

in the state of Sergipe, where the beds were first observed, has lately been found to contain fossil ferns and other land plant remains.

A small collection of these fossils, made on fazenda Jacú near the village of Aracy, has been examined by David White and pronounced to be of Permian age.

This is the first recognition of beds of Permian age in northeastern Brazil.

The rocks of the series are sedimentary beds consisting of coarse basal conglomerates, coarse red false-bedded sandstones, and red and gray shales, pink and other limestones; some of the upper limestones contain much chert.

The Estancia beds cover large areas in the states of Bahia and Sergipe and in the southern corner of the state of Alagoas.

In some places the series rests upon the old crystalline complex of northeastern Brazil; in others it rests unconformably upon or against the Lavras beds which are probably of Carboniferous age, or against the Caboclo shales, which are supposed to be of Devonian age.

Besides the fossil plants from the shales near Aracy described by David White in the accompanying paper, some of the limestone members of the series contain fossil remains of minute algæ. The fossil algæ have been found at many places over the plateau country in the America Dourada region northwest of Morro do Chapeo, state of Bahia.*

The Estancia series includes both marine and land or freshwater deposits.

If the determination of the Estancia beds as Permian is correct, there is an enormous break, representing a long land period, between the Carboniferous and the Permian in northeast Brazil.

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*J. C. Branner: Aggraded limestone plains of the interior of Bahia, etc., Bull. Geol. Soc. Amer., xx, 189–191, 1911.

ART. LIV.—*A New Fossil Plant from the State of Bahia, Brazil*; by DAVID WHITE.

IN the summer of 1911 the writer received from Dr. J. C. Branner a small package of fossil plants collected at Fazenda Jacú, four miles northeast of the village of Araçy, and twenty eight miles north of Serrinha, State of Bahia. The material is of two kinds: (1) several pieces of very imperfectly preserved fossil wood in which the greater part of the space once occupied by the tissues is now replaced by fine-grained ferruginous sand, rendering the material of no paleontological value; (2) four small fragments of rather fine-grained, ash-colored, clay shale containing small flakes of mica, and slightly tinged with purple. These fragments, the two largest of which are shown, natural size, in figures 1 and 2, hold numerous pieces of the pinnæ of a fern-like type associated with but not attached to a portion of a small stem or rachis. The latter is now partly carbonized, being represented by a very thin layer of coal, the greater part of the plant substance having rotted. The laminæ of the fronds are likewise carbonized and are represented in the specimens by a dull, minutely granular, coaly residue, the topography of which is that of the original plant. The carbonaceous residue is apparently spongy, and the pinnæ were evidently somewhat macerated. For these reasons the nervation is best seen in those impressions from which the carbon has been removed.

When the specimens were received from Doctor Branner, there being no rocks older than Cretaceous known throughout the extensive region including the plant locality, the fragments were at once placed for examination in the hands of Dr. F. H. Knowlton, the specialist in the post-Paleozoic floras, in the U. S. Geological Survey. Later they were returned by Doctor Knowlton for the reason that he did not regard them as representing any known type of Mesozoic or Tertiary plants, the aspect of the specimens being rather that of the Paleozoic genus *Alethopteris*.

The general form and appearance of the pinnæ are fairly well shown in the fragments on the two pieces of shale photographed as figures 1 and 2. Several small pieces of pinnæ on the two smaller fragments of shale are not illustrated. These show the pinna to be probably linear, tapering to a narrow acute apex. In some fragments, like that shown in fig. 2, the pinnules are close, while in others, such as the portion seen in fig. 1, they are somewhat distant. The rachis, which is occupied by a much denser carbonaceous residue, is irregularly

Fig. 1.

Fig. 2.

Figs. 1, 2, natural size. *Alethopteris Branneri*, n. sp.

Fig. 3.

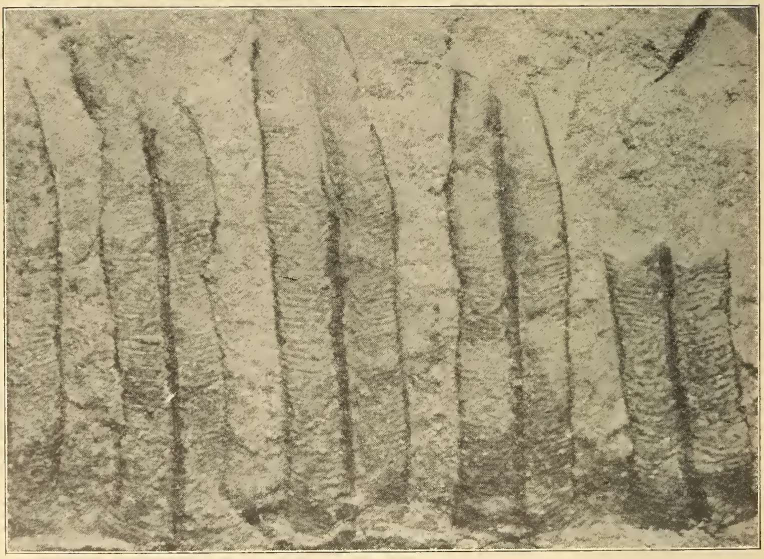

Fig. 3, enlarged.

lineate, and deeply depressed, so that it is considerably below the plane of the ventral surface of the pinnules. The latter vary in position from opposite to alternate, and are distinctly Alethopteroid in form and arrangement, being connivent at the base, open nearly at right angles to the rachis, and strongly convex ventrally on either side of the very thick midrib, which is persistent, vanishing very abruptly just before reaching the apex. In some of the fragments the pinnules appear to be hardly decurrent, the midrib originating at nearly a right angle with the rachis. Likewise in the large fragment there is very little indication of decurrence in the lamina bordering the rachis between the pinnules, but in the small fragment on the upper right in fig. 2, the typical decurrent Alethopteroid wing and the downward direction of the sinus may be observed.

On account of the density of the coaly residue and the degree of maceration undergone by the lamina it is difficult satisfactorily to describe the nervation which may be seen in the impressions of the pinnules. The nerves originate for the most part slightly oblique to the midrib or rachis, though in many cases they appear to emerge at right angles to the latter. They are in general close and nearly parallel, usually forking near the base, one of the divisions being rarely forked, though a large number of the nerves appear to run simple from the midrib nearly straight to the margin, which they meet slightly obliquely or nearly at a right angle. When examined closely under the lens the nervation of many of the pinnules is found to have the aspect of being polygonally meshed throughout a narrow zone near the midrib. At certain other points where the preservation is apparently better, as shown in fig. 3, the nerves appear to be straighter, more nearly parallel, without anastomosis. It is almost certain that they do not anastomose, though occasional meshing is possibly present. The aspect of meshing may be due to maceration of the lamina, in which the mesophyll was apparently thick and the epidermis probably coriaceous.

For the reasons above explained I am disposed provisionally to regard the nerves as probably entirely free rather than in part anastomosed near the midrib, and, therefore, I tentatively refer the plant to the genus *Alethopteris*, a strictly artificial or form-genus of Cycadofilices, with which the Brazilian fragments in other respects fully agree. The species is named *Alethopteris Branneri*, in honor of the donor, who, in coöperation with Dr. Derby, the Director of the Brazilian Geological Survey, has contributed so largely to our knowledge of the geology of Brazil.

The agreement of the Brazilian fragments, so far as concerns their general aspect, with several species of *Aethopteris* is at once apparent from an inspection of the figures. Mention may in particular be made of *Alethopteris aquilina*, and some of the narrowest-pinnuled portions of the pinnæ of *Alethopteris grandini*. The nearest resemblance of the specimens in hand is, however, with the latest Paleozoic representatives of the genus, such, for example, as *Alethopteris Virginiana* F. & I. C. W.,* from the Dunkard formation in southwestern Pennsylvania and northern West Virginia. The later species of the genus are specially characterized by the more open and less decurrent pinnules and midribs, the generally thick texture of the lamina, and the close, very open, and often simple nervation.

The species described above presents a strong superficial resemblance to fronds from the Raniganj coal field (Permian?) of India, described by O. Feistmantel as *Alethopteris phegopteroides*. Our plant differs, however, from the specimen so beautifully illustrated in Part II, vol. III of the Memoirs of the Geoical Survey of India (p. 81, pl. xviii–a, fig. 1) by the less crowded and more tapering pinnules and the more open nerves. The nervation of the Indian specimen is simple.

Regarding the age of the beds from which the fragments here described were obtained, we have no other evidence than that presented by the fossils themselves. Beds of Cretaceous age are known in the general region, but the frond fragments submitted by Doctor Branner come from a formation and series of unknown age. If the fragments are correctly, as I believe, referred to *Alethopteris*, the plant beds may be assumed to be Paleozoic and very likely Upper Coal Measures or Permian in age. The evidence for any age is very scant: but so far as it goes it appears to point toward the Carboniferous period. Pending the collection of additional material showing not only the true character of the nervation of *Alethopteris Branneri*, but also bringing to light other types, the question of the age of the plant bed should be treated with extreme caution, for although fronds of an Alethopteroid aspect are very rare in the Mesozoic, but few forms even resembling the plant in hand having hitherto been described,† it should not be forgotten that similar types may, nevertheless, have been present in South America, and that fronds presenting a superficial similarity to *Alethopteris* are present among living species of Pteris, Mertensia, Aspidium, and other genera.

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*Second Geol. Surv. Pa., Rept. of Progress PP, p. 88, pls. xxxii and xxxiii.

†The fragments described are slightly suggestive of that figured by Nathorst as *Pecopteris Angelini* from the Rhetic of Scania. (K. Svensk. Vetensk. Akad., Handl., vol. xvi, No. 7, 1878, p. 12, pl. I, f. 7.)

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *A New Colorimetric Method for Titanium.*—Lenher and Crawford have applied thymol in concentrated sulphuric acid to the determination of titanium. The reddish yellow to red color is proportional to the amount of titanium present. As thymol itself gives a color when dissolved directly in sulphuric acid, it should be first dissolved in a little acetic acid, and then concentrated sulphuric should be added. The ratio of thymol to titanium may vary greatly, but it has been found best to have at least ·006 g. of thymol present to every ·0001 g. of TiO_2. The test should be made in the presence of strong sulphuric acid, for when the strength of this acid is below 79·4 per cent the color fades in a regular manner with the dilution. The color should be observed at room temperature, for it becomes paler with rise in temperature. Fluorine has a bleaching effect upon the color, but hydrochloric acid, phosphoric acid, and tin did not show any effect. Tungstic acid, on the other hand, increases the color in direct proportion to the amount of tungsten present. The titanium-bearing material is usually most conveniently brought into solution by fusing with potassium acid sulphate. The fusion is taken up in concentrated sulphuric acid, thymol in sulphuric acid is added, and after diluting with sulphuric acid to a definite volume the color is compared in a colorimeter with a standard titanium solution. The test-analyses given by the authors show excellent results, and the method appears to be rapid and convenient.—*Eighth Internat. Congress of App. Chem.*, vol. i, p. 285.

H. L. W.

2. *The Determination of Carbon by Combustion in Moist Oxygen.*—S. Hilpert calls attention to the fact that, while it has been known for a long time that the presence of moisture facilitates combustion, the presence of this agent is purposely avoided in analytical operations. He has found that certain carbides of magnesium and manganese were only slightly oxidized when heated for a long time at a bright red heat in dry oxygen, but the combustion was easily completed when the oxygen was passed through a wash-bottle containing water before it entered the combustion tube. The presence of moisture did not interfere with the determination of carbon, as a good calcium chloride tube was placed in front of the potash apparatus. He has found this method applicable to the direct combustion in oxygen of iron and steel alloys, where the combustion goes on much faster and at a lower temperature with moist than with dry oxygen. Also in elementary organic analysis it has been found that difficultly combustible substances may be much more easily burnt in moist oxygen. In cases where hydrogen is to be determined as well as

carbon, the operation is conducted in the usual way until the hydrogen has been oxidized, then the calcium chloride tube is changed, and the residual carbon is burnt in moist oxygen.—*Berichte*, xlvi, 949. H. L. W.

3. *The Heat of Combustion of Diamond and of Graphite.*—ROTH and WALLASCH have made new determinations of these constants and give the following results :

Diamond	7869 ± 3 cal. per g.
Graphite	7854 ± 1 " " "

The result for diamond agrees closely with that of Berthelot and Petit, but these older investigators obtained a much higher value, 7901–7902 cal., for blast furnace graphite. The new result for graphite represents the higher values obtained by the investigators from several samples of the natural substance and the Acheson product. Other samples of natural graphite gave results no higher than 7830–7835 cal., agreeing with remarkable closeness with the result of Mixter, 7831 cal., published in this Journal in June, 1905. It appears, therefore, that the heat of combustion of diamond is higher than that of graphite, although for a long time the opposite has been supposed to be the case.—*Berichte*, xlvi, 896. H. L. W.

4. *Manual of Qualitative Analysis;* by W. F. HOYT. 12 mo., pp. 36. New York, 1913 (The Macmillan Company. Price 80 cents net).—This very small book gives very brief directions for the detection of single elements and radicals by means of reagents and in the dry way. Such a course, where separations and interferences are left out of consideration might be very useful to beginners, and it is to be remembered that Fresenius gave such a course as a preliminary to more elaborate investigations in his classical work on the subject. But, unfortunately, the book under consideration contains many mistakes and misleading statements. For instance, it is impossible to detect aluminum in the manner described, by adding ammonia to the potassium hydroxide solution ; cobalt sulphide is incorrectly assumed to be insoluble in nitric acid, and thus to be distinguished from nickel sulphide ; in testing for an ammonium salt with platinic chloride, the addition of potassium hydroxide to the liquid is curiously specified. The table of solubility at the end of the book has an astonishing number of mistakes. For instance, ammonium arsenate, ammonium borate, and even ammonium carbonate are indicated as sparingly soluble in acids. In this table the author gives the meaning of the symbols "a" and "w" incorrectly as *slightly* soluble in acids and water. He should have omitted the word "slightly," which gives a meaning practically opposite to the true one. Taking these errors with many others, there are probably more than 200 false statements in this single table of solubilities. H. L. W.

5. *A Course in General Chemistry;* by WILLIAM MCPHERSON and WILLIAM EDWARDS HENDERSON. Large 8 vo., pp. 556. Boston 1913 (Ginn & Company).—The authors state that the text presents few novelties either of arrangement or method.

The most noticeable departure from the conventional arrangement is the postponement of the halogen elements to a relatively late chapter, which the authors consider an improvement. The book appears to present the theories, facts, and applications of chemistry in an excellent manner. The ionic theory is clearly explained, but it is not used obtrusively. The spelling is agreeably conservative, except that "sulfur" is used for sulphur. It may be regarded as one of the best of the recent works on the subject. H. L. W.

6. *Simplification of the Zeeman Effect.*—The "normal" magnetic resolution of spectral lines, which was predicted by the theory of H. A. Lorentz, has been found experimentally only for the lines of helium and for a relatively small number of single lines of cadmium, calcium, magnesium, mercury and zinc. In the majority of cases, however, the spectral lines have shown widely different and very complicated "anomalous" types of separation in the magnetic fields used. These anomalous cases could not be accounted for by a single hypothesis, so that the subject has become more and more involved and confused as experimental data have been gathered. Fortunately, a great step in advance has been made by F. PASCHEN and E. BACK. These investigators used a special form of vacuum tube in order to obtain a source of light of sufficient intensity in very strong magnetic fields. The material of the tubes was fused quartz. Also a specially constructed Klingelfuss induction coil was required to produce secondary discharges of adequate strength and potential difference. With this apparatus it was possible to obtain fully exposed negatives of the more intense lines of hydrogen and oxygen in one hour, using the first three orders of a Rowland grating of the largest size. Helium required only a few minutes exposure in the fifth order. The gas pressure was higher than is ordinarily used in Geissler tubes, its value being 5^{mm} in the case of oxygen. In the second part of the paper, which deals with lithium, potassium and sodium, Back employed alloys of these metals.

A typical example of the results obtained is afforded by the oxygen triplet whose components have the wave-lengths 3947·438, 3947·626 and 3947·731, corresponding to zero field strength. When the magnetic field had a strength of 2800 gauss each component of the triplet widened. At 6187 gauss the three lines were much broadened but still distinctly resolved. At 7738 the edge of the longest wave-length component nearer to the middle line of the triplet was strengthened. At 10930 a central line appeared while the 3947·626 line vanished. At 12770, 21830 and 27880 gauss various changes took place in the "wisps" which developed from the 3947·731 line. Also the shortest wave-length component of the original triplet gradually disappeared with the production of wisps. Finally, at 31900 gauss the outer components of the triplet had vanished altogether. There remained a sharp, intense line in the position of the center of gravity of the triplet. The accompanying wisps were very faint. All of the preceding results involve simultaneously the vibrations parallel and perpendicular to the magnetic field. At 32430 gauss, when the perpendicular vibrations alone were photographed, the two diffuse wisps remained while the central sharp component was absent. Also, at 32000 gauss, when only the parallel vibrations were transmitted, the two lateral wisps disappeared absolutely but the central, resultant line remained sharp and intense. Thus, the original triplet has been reduced to a single line which is completely polarized. It is, therefore, evident that the important discovery of Paschen and Back consists in showing that the anomalous Zeeman effect exhibited by close doublets and triplets can be reduced to the normal type by using sufficiently strong magnetic fields. Of great theoretical moment is likewise the fact that the polorization becomes complete.

In a later paper A. Sommerfeld has discussed mathematically a hypothetical model which accounts for most, but not all, of the phenomena observed by Paschen and Back. Instead of considering the electromagnetic behavior of a single electron which is bound to its position of rest in an isotropic manner (Lorentz), Sommerfeld imagines a quasi elastic *anisotropic* bonding for the electron. He also assumes that the three corresponding frequencies, n_1, n_2, n_3, are not very different in value. The last hypothesis conforms to the cases of close doublets and triplets. It is then shown that the anisotropic electron will approach asymptotically a condition in which it will behave, with respect to its mean frequency of vibration, precisely like the usual isotropic electron, as the magnetic field is increased in strength.—*Ann. d. Phys.*, No. 15, 1912, p. 897; No. 4, 1913, p. 748.

H. S. U.

7. *The Spectrum of Helium Canal Rays.*—It has been shown by J. J. Thomson that helium ions may be present in the canal rays which have one and also two positive charges due to the loss respectively of one and two electrons. The problem of the connection between these singly and doubly charged ions and the spectral series of helium has been successfully investigated by J. Stark, A. Fischer and H. Kirschbaum. Since the argument is long and involved it will not be possible to reproduce it in this place. It may be stated, however, that the authors found it necessary to study the Doppler effect, not only in pure helium, but also in helium mixed with iodine and with oxygen. The most important conclusions are the following: The principal series and the two subordinate series of doublets of helium have as carriers the positive, singly charged ions, while the principal series and the two subordinate series of simple lines have the positive, doubly charged helium ions as carriers. The series of single lines were formerly ascribed by Runge and Paschen to a hypothetical element which they called "parhelium." Although this gas does not exist in the chemical sense of an element which can be isolated, it is interesting to note that its spectrum has been accounted for in a perfectly satisfactory manner.—*Ann. d. Phys.*, No. 3, 1913, p. 499. H. S. U.

II. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *The National Academy of Sciences.*—The semi-centennial meeting of the National Academy was held in Washington on April 22, 23, and 24. The meeting was very largely attended, more so in fact than on any previous occasion, upwards of seventy members being registered. The customary order of events was deviated from in that the usual reading of papers by members of the Academy was omitted, and a number of formal addresses given by invited guests. President Remsen opened the meeting on Tuesday and was followed by President A. T. Hadley, who spoke on "The Relation of Science to Higher Education in America." Other addresses given on Tuesday were on "International Coöperation in Research" by Dr. Arthur Schuster, Secretary of the Royal Society of London, and on "The Earth and Sun as Magnets" by Dr. George E. Hale. On Wednesday the program contained the following: "On the Material Basis of Heredity" by Dr. Theodor Boveri of Würzburg; and "The Structure of the Universe" by Dr. J. C. Kapteyn of the University of Groningen.

On Wednesday afternoon, the members of the Academy and guests were received by the President at the White House, upon which occasion the Draper medal was presented to M. Henri Deslandres, the Watson medal to Dr. J. C. Kapteyn, and the Agassiz medal to Dr. Johann Hjort; also the Comstock prize to Prof. R. A. Millikan. Thursday morning was given to the election of new members, as noted below. In the afternoon an excursion was made on the "Mayflower" to Mt. Vernon. There was a reception on Wednesday evening at the Carnegie Institution, and a dinner for the members of the Academy on Thursday evening. The lists of the members and of the foreign associates elected are as follows:

Members: Henry A. Bumstead, Yale University; Leonard E. Dickson, University of Chicago; Ross Granville Harrison, Yale University; Gilbert N. Lewis, Massachusetts Institute of Technology; Armin Otto Leuschner, University of California; Lafayette B. Mendel, Yale University; George H. Parker, Harvard University; Louis V. Pirsson, Yale University; Edward B. Rosa, Bureau of Standards; Erwin F. Smith, Bureau of Plant Industry.

Foreign Associates: Theodor Boveri, Würzburg; William Crookes, London; Gaston Darboux, Paris; Henri Deslandres, Meudon; Albert Heim, Zurich; Albrecht Kossel, Heidelberg; Karl Friedrich Küstner, Bonn; Arthur Schuster, London; Johannes D. van der Waals, Amsterdam; August Weismann, Freiburg; Max F. J. C. Wolf, Heidelberg.

Dr. William H. Welch was elected President of the Academy, Dr. Charles D. Walcott, Vice-president and Dr. Arthur L. Day, Secretary.

2. *List of North American Land Mammals in the United States National Museum*, 1911 ; by Gerrit S. Miller, Jr. Pp. xiv, 455. Washington, 1912 (Smithsonian Institution, United States National Museum, Bulletin 79.)—The author has made a minute study of the mammals, not only of North America, but of Europe as well, and he now presents a summary of the systematic results of study in this field to the end of 1911. The geographical area covers the entire North American continent from Panama and the Greater and Lesser Antilles northward, and also includes Greenland. It is interesting to be informed that no other museum contains so rich a mammalian fauna for an equally large area. For example, the total number of forms recognized is 2,138, of which only 183 are not represented. The collection as a whole numbers some 120,000 specimens, including 1,135 types. The catalogue is especially valuable in connection with a similar work on Western Europe prepared by the same author, under the auspices of the British Museum.

3. *An Index to the Scientific Contents of the Journal and Proceedings of the Academy of Natural Sciences of Philadelphia.* Published in Commemoration of the Centenary of the Academy, March 21, 1912. Pp. xiv, 1419. Philadelphia, 1913.—The fifteenth volume of the Journal of the Academy of Natural Sciences of Philadelphia, commemorating its one hundredth anniversary on March 21, 1912, was noticed in the February number (p. 199). A second publication, no less important although less original in subject matter, has now been issued through the efforts of the recording secretary, Dr. Edward J. Nolan. This is an Index to both the Journal and the Proceedings of the Academy since their beginning. It is divided into two parts: The first, pp. 1–187, gives a list of contributors with the titles of their papers ; the second, pp. 189–1419, is a complete index of genera, species, and the subject matter in general. The magnitude of the task, recorded in this weighty volume, is obvious at a glance, but the amount of labor involved can hardly be appreciated by one who has not taken active part in such work. It may be interesting to add that five years after the founding of the Academy, that is, in 1817, the First Series of the Journal in octavo was begun ; the Second Series of the same in quarto was inaugurated in 1847 and the last volume, XV, is alluded to above. In March, 1841, a series of Proceedings was begun of which the sixty-second volume, the last included in this index, was completed in 1911.

OBITUARY.

Professor William M. Fontaine, for more than thirty years professor of natural history and geology in the University of Virginia, died on April 30 in his seventy-eighth year. He was especially distinguished for his researches in paleobotany, published under the auspices of the U. S. Geological Survey, in the pages of this Journal and elsewhere.

Professor Lester F. Ward, professor of sociology in Brown University and earlier geologist of the U. S. Geological Survey, died on April 18 in his seventy-second year. His geological work was particularly in the department of paleobotany.

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*This Index contains the general heads, CHEMISTRY, GEOLOGY, MINERALS. OBITUARY, ZOOLOGY, under each of which the titles of Articles referring thereto are included.

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