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No. 11,726.

June 7, 1894 - June 11, 1896.

JOURNAL

OF THE

Elisha Mitchell Scientific Society

VOLUME XI—PART FIRST

JANUARY--JULY

1894

POST-OFFICE :
CHAPEL HILL, N. C.

ISSUED FROM THE UNIVERSITY PRESSES,
CHAPEL HILL, N. C.
1894.

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THE LONG LEAF PINE AND ITS STRUGGLE FOR EXISTENCE.

BY W. W. ASHE.

As a country increases in population the relative area of its woodland and forests, from which both timber and a large part of its fuel must be drawn, decreases in like or even greater proportion. The care and propagation of timber trees *en masse* becomes a feature of economic administration; and in all cases the inauguration of the policy of forest cultivation has emanated from the government. The cause of this dependence on the government for the initiation is patent. Although individuals may see, as forest materials become scarcer, that some definite plan, in regard to forest management, should be followed, they are, as a body, unable to put on foot a general line of action which will in any measure tend to increase the supply.

This inaction of individuals is due to two causes: (1) A disregard for the future, since the benefit of any reform, or at least the realization of increased income from any reform which may be made in the management of forests will be derived only after many years; broadly speaking will be of advantage only after the

passing of a generation. For this same reason there is an increasing tendency to cut all marketable trees, even of the smallest size, that returns may be had at once.

(2) Even when some desire is evinced to so care for woodland that the return therefrom may be regular and the condition of the woodland may not deteriorate, either in respect to average size or choice of trees, there is great ignorance shown of all requirements for tree growth and of the action demanded to secure desired results.

The larger and more thickly settled European governments, recognizing these facts, have many years ago undertaken to place all their own forest lands under systematic management and at the same time supply, by means of their schools of forestry, the knowledge of these methods to private land-holders or to trained officers who may serve them. In many of these schools series of experiments, analogous to those made upon grains, etc., in the Agricultural Experiment Stations of the United States, have been carried on upon forest trees, to determine the conditions of light, soil, moisture and density of tree growth which they require for their best development, and the age they should be allowed to reach before cutting, the diseases, fungous and other, to which they are subject, their destructive insects, and the trees, naturally and those most advantageously, associated together in forests.

What has been done by these governments for their forests will have to be repeated in modified forms by the federal and various state governments for their respective forests as soon as the great bodies of standing timber which have required the uninterrupted efforts of centuries to accumulate, are destroyed or thinned

out. Conditions will be presented analogous to those experienced in Europe and these must be treated along the same lines and finally resolved by the application of similar methods and by considering the general effects upon our trees of their environments, the soils, atmospheric changes and the various forms of plant and animal life. It will be understood from this how necessary it is that the pathological characteristics of trees worthy of extensive culture for their timber, should be known.

As yet we are in the dark about the demands of even our more common trees. As a people it has scarcely become known to us that our forests are exhaustable, much less that there are large waste areas, now entirely unproductive of commercial timbers and that these areas less than fifty years ago were wooded, in some instances heavily wooded, with valuable trees. There are such tracts of waste land in North Carolina in what are known as the "pine barrens" of the eastern counties. In the course of an examination of the timber lands of eastern North Carolina undertaken last year (1893) by the North Carolina Geological Survey some inquiry and research was made into the extent of these waste areas and a more extended discussion of the results of this examination will be found in Bulletin 3, of the North Carolina Geological Survey, now being published. These areas were found to include considerably over 400,000 acres and to be increasing so rapidly that the causes leading to them were sought for. This entailed an analysis of the life history of the long leaf pine and of the other pines with which, in this region of North Carolina, it is most intimately associated. While these observations are by no means either exhaustive, or even full, they will show in a general way

with what difficulties a tree has to struggle, under the changed condition of civilization, in order to grow up and reach maturity. They also show the pressing need for a more efficient, or at least common sense, method of dealing with our forest lands if there are in the future to be any forests.

A brief statement of the facts noted in regard to these pine lands, summarized from the same bulletin, will serve to show the deplorable condition of these lands at the present time and how they were when covered with virgin forests.

There are four pines found in the eastern section of North Carolina. Only two of these are, however, generally enough distributed to be of economic importance. These are *Pinus palustris* (Miller) the long leaf pine and *Pinus taeda* (Linné) the loblolly pine, called in eastern North Carolina short leaf or old field pine. The loblolly pine has numerous close allies in eastern America and Europe, though it is a very distinct tree from any of these. Its growth in the virgin forest is confined to the wet margins of the swamps, to "hammocks" in the swamps and to the moister lands with sand or loamy soils, even when sometimes immersed.

The long leaf pine has in North Carolina reached the farthest northerly extension of any pine in its subsection of the genus *Pinus*. Taking the sum of like morphological characters as expressing the greatest relationship and starting with the white pines, which are the most northerly distributed pines of America, it will be found that the sub-section of the genus *Pinus*, to which the long leaf pine belongs, is farthest from the white pines, *i. e.*, has fewer like characters in common, and at the same time has the most southerly extension of any pines of America. The congenitor of

the long leaf pine is the Cuban pine, *Pinus cubensis* (Goert) which is found in Florida, Georgia, and the West Indies, while other nearly allied species are found in Mexico and the tropics.

Byrd, Lawson,* and the other early historians and eulogizers of eastern North Carolina unanimously assert that the long leaf pine extended over all the higher sandy land from Nansemond county, Virginia, southward. It was abundant in Hertford, Perquimans and Gates counties, where a tree of this species is rarely ever seen now, and through Bertie county which was then called the "Pine Forest" and which is now covered with a heavy growth of loblolly pine. Long leaf pines must have been common in the Pamlico peninsula as tar kiln mounds, now covered with large trees of other species, are frequently seen as one rides along the road. Within the last fifty years the upland forests of Wilson, Edgecombe and the northern section of Wayne counties were composed almost entirely of long leaf pine, while at the present time the loblolly pine has gotten possession of this land wherever the soil was sufficiently moist to support the growth. South of the Neuse river over the rolling dry sandy soil of the "pine barrens" the long leaf pine held undisputed possession. These lands are too poor and dry for the loblolly pine to grow upon until the soil has been cultivated and fertilized. The only tree which disputed the control of these lands, with the long leaf pine, was a small oak, the sand black jack oak, *Quercus catesbevi* (Michx) which is worthless for all timber purposes. As the long leaf pine after having been worked for turpentine was burnt off of these tracts or was cut for

* Byrd writing in 1728, Lawson in 1701.

lumber, the only tree which replaces it was this sand black jack oak.

These waste tracts, either naked or covered with the sand black jack oak, lie south of the Neuse river and are to be found in every county from New Hanover westward to Richmond and Moore. It was with a view to ascertain the feasibility of restocking these lands with a valuable tree and preventing the enlargement of these waste acres that this examination was made of the habits, characteristics and relative adaptability to existing conditions, both natural and artificial, of these two pines, *Pinus taeda* and *P. palustris*.

THE CAUSE OF THESE WASTE LANDS.

From the preceding it appears that there is a large amount of waste land lying in the southeastern part of this State. There are now over 400,000 acres of such land, and the amount of it, from various causes, is constantly increasing. This land consists of high rolling or hilly sand barrens, formerly covered with extensive forests of long leaf pine. These forests yielded turpentine abundantly, but on account of the larger amount of sapwood and the coarser grain of the wood of trees growing on these poorer sandy lands the lumber, though of good quality, was of a grade inferior to that from trees grown on fertile soils. Now, however, owing to the grossest neglect, large portions of these forests have either been destroyed entirely or reduced to such a condition that there is neither mill nor turpentine timber on them, and no regrowth of the long leaf pine has been allowed to take the place of the older trees as the latter were being gradually exterminated. The soils of the barrens on account of their

sandiness and poor quality will produce very few kinds of trees which have any economic importance. No valuable broad leaved trees (oaks, etc.) thrive on these lands, and among the conifers (pines, etc.) the long leaf pine is the only one growing naturally on them. The short leaf pine, where the loam sub-soil lies near the surface, is rarely found, and it is only after the ground has been cultivated and enriched and the moister layers of earth have been brought to the surface that the loblolly pine will grow there. So it seems that the long leaf pine is the only native tree of much value which flourishes on these barren sandy lands. There are very few, if any other, forests in the eastern United States so peculiarly limited as to the variety of valuable tree growth as the long leaf pine forest, particularly when it grows on the sand barrens, and there are no other forests which demand such care to obtain a regrowth of the original dominant species. Many kinds of trees after being lumbered or burnt out are succeeded by smaller and less valued species, but the original growth in time again takes possession of the land. This is the case with the spruce forests of western North Carolina, and the white cedar (juniper) in the eastern section of the State. However it may have been primarily in the long leaf pine forests, this is not the result under the present management of these pineries. After the removal of the pine the land quickly becomes waste land, and passes from a growth of sand black jack to utter barrenness. No where is there any general sign of either the long leaf or any other pine again forming a prominent part of the growth on these sand hills.

Unless there is some radical change in their management, these lands may even cease to produce the few

sand black jack oaks which now flourish on them. There is even a possibility and in fact it can be said a great likelihood that this valuable tree, the long leaf pine, will become extinct in North Carolina unless some steps are taken to secure its more general propagation. It has already become extinct over large tracts lying to the north of the Neuse river which were formerly occupied either exclusively by this pine or by mixed forests of it and hard woods and loblolly pine.

THE REASON WHY LONG LEAF PINE FORESTS ARE NOT SELF PROPAGATING.

The causes which have operated to prevent the long leaf pine from propagating itself are several, and all of them are important and act uniformly throughout this sandy area. A brief statement of some of the peculiarities of this tree may enable us to see more clearly why it needs more special protection than must necessarily be accorded other trees to enable the forests to reproduce themselves. The chief causes which have influenced and tended to retard the general regrowth of this tree at the present time arise from a highly specialized form of seed and plant structure and a decidedly unique manner of growth when compared with the other pines of this same region. These characteristic peculiarities lie chiefly in the young pine seedling, in the seed, and the structure of the leaf buds.

THE SEEDING OF THE LONG LEAF PINE.

Although the writer has not yet carried on systematic observations, on (1) the frequency of seeding of the long leaf, (2) the relative abundance of its seed as com-

pared with those of other pines, and (3) the fertility of boxed and unboxed trees of the same species, long enough to have obtained accurate results, yet the observations of different persons, thoroughly familiar, for many years, with the pine of the barrens, will, he thinks, for most of these cases be found sufficiently accurate, their results being supplemented by his conclusions drawn from a personal investigation extending over several years. Although there were certain years in a virgin long leaf pine forest, just as there are with all other trees, when there was no seed borne, yet these were rare and the yield of seed was usually abundant. Wm. Byrd, writing in 1723, says:* the mast of this tree is very much esteemed for fattening hogs through all of Albemarle County, (North Eastern North Carolina) on account of its greater abundance and the greater certainty of its occurrence (than that of the oaks). The forests of which he was speaking were largely virgin at that date. There are to be found frequent statements mentioning the same fact by other historians, of both an earlier and later date.

So far as could be ascertained the masts (as the seeds of this pine are called) have not been as abundant for the past fifty years as they formerly were. There seems to have been only three large long leaf pine masts since 1845. One of these occurred just about that time, the next one was in 1872 and there was one in 1892, which was not as large, however, as either of the preceding. There is a fairly abundant mast about every four or five years, and on intermediate years the production is small and localized. In North Carolina most of the trees which now bear seed are boxed and have been in this condition for from 50 to 100 years,

* History of the dividing line between Virginia and North Carolina, p. 29.

and the opinion prevails throughout the pine barrens that pine masts are less frequent and less abundant now than before the pines were so largely boxed and thinned out. The removal of a great part of the trees may explain, in part or wholly, why masts are less abundant. It would naturally be inferred that there would be a large decrease in the productiveness of boxed trees, whose vitality, measured by the rate of accretion between them and unboxed trees, has been greatly impaired by the practiced manner of boxing. However, from a tabulated record of observations carried on during several years, there as yet appears no marked difference between the productiveness of boxed and unboxed trees, similarly situated.

There are several important differences between the reproductive capacities of the loblolly and long leaf pines, all of them to the advantage of the loblolly pine.

The fertility of the long leaf pine is much less than that of the loblolly pine, its most frequent associate. The loblolly pine bears cones at an earlier age, and usually produces more seed, both perfect and imperfect ones, and the great variety of soil, on which the loblolly pines grow, causes a slight difference in the time of flowering of different trees, making this pine less liable to have the entire prospect of a seed yield destroyed by frosts or by heavy rains during polination. While this may possibly explain why the loblolly pine has come up as a regrowth over so much of the moister loam land, it has affected the growth of the pine barrens very little.

The seed of the long leaf pine are very large, $\frac{1}{3}$ to $\frac{1}{2}$ an inch long, independent of the wing, while no other pine of this region has seed over $\frac{1}{4}$ an inch long, but there is a smaller proportion of abortive and otherwise

imperfect seed in a long leaf pine cone than in the cone of the loblolly pine. This would be decidedly to the advantage of the long leaf pine in seeding old fields, etc., were its seed not too heavy to be carried far by the wind. They usually fall within fifty feet of the parent tree, while the light winged seed of the loblolly have been known to scatter thickly over fields from trees over a quarter of a mile distant; and single seed are reported to have been blown several miles. Furthermore, as described more fully beyond, the seed of the long leaf pine are much more extensively destroyed by hogs, fowls, squirrels, rats, etc. Another reason for the exclusively loblolly growth in fields may be that even when the seed of the two pines fall on the same land the loblolly pine by its rapid growth during the first few years overshadows and effectually crowds out the more slowly growing long leaf pine; and the latter, during this early slow growth are easily destroyed by fires and by live stock. The two are, however, rarely seen associated together in second growth woods. The seed ripening in October, fall to the ground rapidly and if there is a warm moist season sprout immediately. In the event of a long warm rain just after the seed are matured, they will frequently sprout in the cones and the entire yield will be thus destroyed.

THE YOUNG PLANT.

The young long leaf pine seems to be specially adapted by the form of its root system for growing on a sandy soil. By the end of its first year's growth, its root system, which has grown rapidly, consists of a large tap-root which extends 6 to 10 inches deep in the sand

from the bottom of it branch out the smaller roots which draw nourishment from the soil. It is this deep seated root system, sent thus early far down into the soil, which enables this pine to grow on the sand barrens, and it is doubtless because the roots of the loblolly are small and divide for the first year or two into a great many small divisions, lying near the surface, that it does not get sufficient moisture and nourishment from the dry surface sand to enable it to thrive on the sand barrens before this land has been cultivated. This long tap root of the long leaf pine frequently goes through the sand into the loam soil and secures for the tree a firm anchorage against storms and enables it to draw its nourishment from a more fertile soil. The stem parts of the long leaf pine are as peculiarly adapted for growing on a sand soil as the root system is. Instead of the stem branching or growing the first year, it only puts out a great number of very long thick leaves, exceedingly close to the ground. These leaves soon spread out and help to shade the ground close to the plant and keep it moist. At the end of the first season's growth the single (terminal) bud is not over an inch and a half above the earth and the bud itself is nearly an inch long, so that it can be said that the stem of the seedling does not grow any in height during the first year, all the energy of the plant being diverted to increasing the root and producing the great tuft of long deep green leaves which spread out immediately below the bud and make the plant resemble more a tuft of some marvellous kind of grass than a young tree. Some of the lowest leaves usually die during the first year; most of them remain on for two seasons.

The second and third year growth of the stem in height is slight, though it increases in thickness, but

after that, at least in a forest, its growth is wonderful. Frequently in a thick wood where young trees have been allowed to grow, they will in eight or nine years after height growth has begun, have reached a height of 18 or 20 feet and a diameter of no more than three or four inches, and will have grown each year from only one bud, the terminal one, at the end of the woody axis, there being no branches and no sign of any having been formed. For leaves there will be only a single broom like bunch terminating the slender stem. The rapidity with which this stem is raised and the fewness of its branches until the natural height of the tree is reached makes one of the fine qualities of the timber. It gives long stocks which have no knots in them, even small ones, to produce any uniformity of quality or to make weak places on the interior of an apparently perfect piece of timber. This feature which is the cause of so fine a quality of wood is a great drawback to the development of the young trees. This single terminal bud is a very large and complicated structure, and when once destroyed in any way no other bud is usually formed by which the growth of the young seedling can be continued. It is true of most conifers (*i. e.* pines, firs, cypress and cedars) that they do not form buds readily and that they rarely sprout from the stump and are very difficult to reproduce from cuttings, etc., but with the long leaf such buds are formed and sprouts developed even more rarely than with most other conifers.

ENEMIES OF THE LONG LEAF PINE.

The long leaf pine has a severer struggle for existence than any other of our forest trees, for the reason

that in all stages of its reproduction and growth it is more severely and continuously attacked by a greater variety of enemies than any other. Besides the natural drawbacks to its development from the peculiar manner of forming several of its parts, and the fact that these parts when destroyed are not replaced, its large and sweet seed are eaten in large quantities by fowls of various kinds, rats, squirrels, and by swine, which prefer them to all other kinds of mast, and when there is enough long leaf pine mast become very fat on it. If the destruction caused by swine ceased here there would doubtless still be sufficient seed left to reproduce some parts of the forests as the mature trees are gradually thinned out, for one year old seedlings are common 12 months after heavy masts. No sooner, however, has the young pine gotten a foot high and its root an inch in diameter than the hog attacks it, this time eating the roots, which until two inches in diameter, are very tender, juicy, pleasantly flavored and free of resinous matter. In the loose sandy soil the pine woods hog or "rooter" finds little difficulty in following and devouring these tender roots to their smallest ends. Many small trees are destroyed in this way; and cattle, furthermore, are said to frequently bite off the tops of the small plants, and with it the terminal bud, in the early spring. This is doubtless done while grazing, more accidentally than otherwise.

Fires often destroy all the young pines that escape the hogs. They kill the small pines by burning the highly inflammable bracts around the bud and so stop its growth, or in high grass frequently burn all the leaves. Larger trees, even until they are three or four inches through, are easily killed in spring, when the sap is rising and the outer layer of wood is growing rap-

idly, by a hot fire which will burn the thin exfoliated layers of bark all over the trunk. The loblolly pine is less injured by fire because its bark is thicker and so offers more protection to the growing wood,—the bark, too, lying closer to the wood in firmly appressed layers, does not so easily take fire.

So far as has been observed, young long leaf pines are attacked by no injurious beetles or bark borers or by any fungi sufficiently to injure them. The mature pines, however, have in the past years several times been attacked by bark beetles in such numbers as to destroy the pines over large areas. A few trees which have been killed from their attacks can be seen at any time around the edges of districts when lumbering is in progress, or about districts which have been recently lumbered.

The chief agencies, then, which prevent a regrowth of the long leaf pine on the high sandy lands, are the hogs and the fires; and the attacks of the hogs are directed against parts which seem to have been developed to meet requirements of a plant growing on a dry barren soil of loose sand. These peculiarly developed parts are the seed, large for a pine, which contain abundant nutriment for the young plant to enable the root to push itself rapidly into the sand; and then the long succulent root which grows for a considerable distance straight down without branching. Since the first settlement of these sandy lands the "ranging" of swine has been allowed in the forests, and while there were enough pines standing, and frequent masts, they fed a large number of hogs.

The practice of firing the barrens, has been adopted in many cases with a view to improve the pasturage; while in many other cases, after the trees were boxed,

the leaves and trash pulled away from around them, the forests were burned over to prevent, in a dry season, a chance conflagration getting from under control and burning the faces of the turpentine boxes and the timber. That this policy of burning the barrens is a very bad one and calculated to do far greater damage than that immediately apparent has perhaps been made evident. That sooner or later the present management or lack of management which has characterized all dealings with the barrens for the past 140 years, must be changed if the long leaf pine forests are to be made self-propagating, no one who has ever seen their condition, or fully realizes what it is, can possibly doubt. The logical result of these burnings in the past has been the destruction of millions of feet of standing pine and the prevention of the growth of young trees; which, had they started even 50 years ago, would now be large enough for small timber and turpentine trees; while, the burnings of the present and future, if not soon discontinued, will mean the final extinction of the long leaf pine in this State.

NITRIFICATION.

J. R. HARRIS.

The changes which nitrogenous organic matter, or any form of nitrogen, undergo in nature in being converted to nitric acid, or nitrates, is called nitrification. Nitrogen is one of the most abundant, and at the same time most important, elements in nature. More than

three-fourths of the atmosphere around us consists of nitrogen, and it enters as an essential constituent into all forms of animal and plant life. The complex nitrogenous organic compounds found in nature are not assimilated as such, but are in some way formed within the plant from simpler nitrogen compounds taken in through the roots.

When these complex compounds are exposed to the decomposing agencies of the air and soil they readily return to the simpler and most stable forms which can exist in nature. The nitrates, as the last and highest state of oxidation of nitrogen, are known to be the most stable compounds. As an evidence of this, vast deposits of sodium nitrate have been stored up and preserved in the rainless regions of Chili, Peru and other countries, Minute amounts of nitrates are almost universally present in soils and waters. They have been found by many experiments and practical field tests to be the form of nitrogen most acceptable as a plant food and to an application of which they most readily respond. Nitrates would seem to have been indicated by nature as the most convenient starting point for the formation of all nitrogen compounds

A knowledge of their wide-spread existence in nature and the very important relation which they bear to agriculture has long been known. Chemists have performed many experiments and advanced numerous theories as to the manner of their formation. This natural phenomenon was evidently a process of oxidation brought about by means of atmospheric and soil agencies. Simple oxidation was not sufficient to explain the notable nitrate formation in compost heaps and nitre beds. The process was known to be much more active and to take place near the earth's surface. Calcium

carbonate or wood ashes were absolutely necessary and, contrary to all oxidation processes, a limited supply of air gave the best results. Carbonates evidently aided in some way, probably in decomposing the organic matter, but rapid decay hindered the process, and in combustion, which is more rapid oxidation, the production of nitrates was indeed very small. So that chemists puzzled over this apparently inexplicable question for a long time before a true suggestion was offered.

It is only within the past twenty years that a satisfactory theory has been advanced and only within the past three or four years, after the most careful and painstaking experiments by some of the most eminent physiological chemists has the theory been accepted.

A. Muller (*Landw. Versuchs-Stat*, 16, 273. *Jour. Chem. Soc.* 1873, 1267) observing the rapidity with which the ammonia of sewerage and certain waters changed to nitrates and that pure solutions of urea and ammonium compounds were not susceptible to this change, suggested that it was due to the action of ferments. The truth of Muller's suggestion was first shown by the labors of Schloesing and Muntz (*Compt. Rend.* 85, 1018). They studied the action of heat upon the process and soon found that varying temperatures exerted a remarkable influence. A temperature of 100°C. for one hour was sufficient to destroy the nitrifiable power of certain soils and vegetable moulds in which nitrification was known to be most actively taking place. The addition of a little unheated mould however, served to again start the process. This was very strong evidence that nitrification was in some way connected with organized life. A powerful microscope revealed to them the existence of numerous organisms of the most varied kinds, being most abundant in vegetable mould.

Nitrification could be started or stopped at pleasure and was clearly seen to be due to the life action of these micro-organisms. The observations of Schloesing and Muntz were soon followed by the publication of the experiments carried out in the Rothamsted laboratory by R. Warington (J. Chem. Soc. 1878, 44). In addition to confirming the previous experiments of Schloesing and Muntz, Warington added many proofs establishing the ferment theory and showing its relation to nitrification. The results of his experiments extending over a period of about fifteen years (J. Chem. Soc. 1878, 1884, 1885, 1889, 1891) are published with all the minute details. And it is to the labors of Warington more than to any one else that we owe our present knowledge of the nature and results of the life action of these microscopic organisms. The fact that they were really lower forms of life was not generally accepted, though the chain of evidence establishing this theory now seems to be complete. They possess all the attributes of organized life requiring a suitable temperature for their development and suitable food for their existence. The most favorable temperature is about 100° F; above 120° or below 40° they are rendered inactive, and are destroyed at 212°. The presence of organic matter and phosphates are essential. They are destroyed by the action of disinfectants, insecticides, and the presence of any considerable amount of alkalinity is detrimental to their growth. Just as calcium carbonate or wood ashes were required in nitre heaps so it, too, is necessary for the growth.

These organisms are found much more abundant in the surface layers of the soil, a fact which confirms observations, long known to be true, that production of nitrates was mainly confined to the surface. Even in

warm countries where the natives collect the nitrates accumulated as an incrustation on the soil, they are aware of the fact that the efficiency of the bed depends on removing only the upper crust. Warington found the following amounts of Nitrogen as nitrate in two fallow soils at Rothamsted:

In the first nine inches	25.5,	40.1	lbs.
“ “ second “ “	5. 0,	14.3	“
“ “ third “ “	—	5.5.	“

Portions taken at different depths were added to diluted, sterilized solutions of urine containing a little calcium carbonate and gypsum. The formation of nitrates was accepted as evidence of the presence of the organisms. In this way Warington succeeded in detecting their presence at depths of six feet from the surface, below this he was unable to find them. It is especially note-worthy that there was always a period of inactivity followed by a period of activity after the introduction of the soil portions. This he regarded as due to incubation, and the time required was much less in the case of surface portions. We would naturally expect to find any forms of life near the surface, and especially so, since the conditions most essential for their growth exist in greater abundance in surface soils. While Warington's cultures were made in solutions, in which the conditions were not the same as those of the soil, he was better able to control them, and to make the experiments of any desirable composition. But little is known of the way in which they act, only certain products are obtained as a result of the organisms' existence. When a suitable nitrifiable solution is seeded with either a portion of a nitrified solution or of a soil or soil infusion, nitrates are usually produced as the final result. In some cases notable quantities of ni-

trites were formed and they were noticed always to precede the formation of nitrates. This led Warington to suspect the presence of two different organisms. And various attempts were made to isolate them.

The Franklands (P. F. and Grace C.; Chem. News, March 21, 1890) were unable to isolate them by gelatin cultures. The organisms either did not grow on gelatin or, when so grown, lost the power of producing nitrates. They finally succeeded in getting an attenuation, one millionth of the original solution, by means of the dilution method, which produced nitrates in suitable solutions and had the microscopic appearance of bacilli. Warington (J. Chem. Soc. 1891, 484) finally succeeded in isolating the two organisms, the presence of which was indicated by his previous experiments. They are very similar in appearance and belong to the same family. The nitrous organism, isolated through successive cultures in ammoniacal solutions made permanently alkaline with sodium carbonate, and containing phosphates, oxidized ammonia to nitrous acid only; it produced nitrous acid in solution of milk, urine and asparagine, and could apparently assimilate carbon from acid carbonates. The nitric ferment did not produce either nitrites or nitrates from ammoniacal solutions, in fact ammonia hinders its action. It rapidly changes nitrites to nitrates.

Previous experiments of Warington (J. Chem. Soc. 1884, 637) had shown that in all experiments in which nitrogenous organic compounds were used, the formation of ammonia preceded that of nitrites and nitrates.

Warington believed that ammonia was the only nitrifiable substance, and only such substances as were capable of forming ammonia through the action of soil organisms could form nitrates. More recent investi-

gation has shown that the process takes place in at least three different stages, and is probably due to the action of different organisms. Emile Marchal (Bul. Acad. Belgique 1893 (3) 25, 727 abs. Chem. Cent. Blatt. 1894 2, 97) isolated some of the most prevalent soil organisms and studied their action upon organic matter. He was enabled to isolate by means of alkaline gelatin and peptone some thirty different species, all of which changed organic nitrogen into ammonia. Fifteen of the number were energetic in effecting this change. The *Bacillus Nycoides*, one of the most abundant in nature, produced ammonia from egg albumen, legumen and gluten. A temperature of about thirty degrees C. and a slight alkalinity was most favorable to its development. Messrs. A. Muntz and H. Coudon (Ann. Agron. 19, 1893 No. 5 page 209) found that Bacilli, Bacteria, Micro-cocci, and yeasts produced ammonia in sterilized soils from nitrogenous fertilizers. The production of ammonia then is not due to the action of any one species, but a great number of organisms have the power effecting this change. Ammonia once formed passes very rapidly into nitrates. This is shown by the facts that although these organisms are continually producing ammonia, yet only minute amounts of its compounds can be detected in soils. It is also formed in numerous other processes of putrefaction and decay, the greater portion of which escapes into the air to be again brought to the soil by snow, rain and dew. It is, however, generally admitted that plants may absorb some ammonia through the leaves, but the amounts obtained in this way are believed to be very small. When any considerable time has elapsed after a heavy application of ammonium compounds to the soil, only traces are found, whereas nitrates can be detected

in fairly large amounts. Nitrates are continually formed according to Berthelot and Andre (Storer, Vol. 1, pp. 307-8) in certain parts of plants. Here the plant cells promote oxidation in a manner analogous to that of the micro-organism. They prove this by inserting portions of the stems of the amaranth. plant into washed and sterilized soil. After a time a notable nitrate formation had taken place in the soil containing the plant stems, while none was found in other soils similarly treated but containing none of the amaranth. Small amounts of nitrates are formed from the action of electricity upon the nitrogen and oxygen of the air. Rain water collected immediately after a thunder storm invariably contains a greater percentage of nitrates than at other times. There are also various oxidation processes continually producing small quantities of nitrates. They can usually be detected in certain metallic oxides as ferric-oxide and manganese dioxide, though it has not yet been explained in what way these substances aid in the formation. The action of all these agencies is necessarily slow, and some nitrogen is lost to the soil, being given off in the free state. In other changes, too numerous to mention, great quantities of nitrogen yearly return to the air.

There must exist somewhere in nature a means of supplying this deficiency or the visible supply of available nitrogen would annually become less and less. The experiments of Lawes and Gilbert and Pugh in England and Boussingault in France, in which combined nitrogen was excluded by a series of wash bottles, were long ago accepted as proving that a plant could not utilize free nitrogen of the air. Recent investigations show that this is not true of leguminous plants when aided by the action of certain soil organisms. It is be-

lieved by some that the equilibrium between free and available nitrogen is in part preserved in this way. When leguminous plants are grown under normal conditions there are formed upon the roots small nodular or wart like protuberances varying in size from that of a pin head to a pea. They are generally called tubercles. Microbes are found associated with all tubercles, and are plainly the cause of their formation. Leguminous plants, when grown in sterilized soil, have no tubercles and require nitrogenous food for their growth. If soil infusions are added to the cultures in sterilized soil, tubercles are formed and the plants thrive without the addition of nitrogenous manures. It is then clearly not an inherent power of the plant, but depends upon the presence of the tubercles, which are caused by the soil organisms. Atwater and Woods (Conn. Station Ann. Report, 1889), found in a series of eighty nine experiments that, in all cases, where there was tubercular formations there was also an increased gain of nitrogen, being the greatest where there was the greatest number of tubercles. So far as our present knowledge extends root tubercles are confined to the Leguminosæ. They are readily produced on the roots of any member of this family, either by inoculation, the addition of small portions of crushed tubercles, or soil infusions containing the organisms. The concurrent opinion of all the investigators of this subject is that the formation of tubercles is caused by the soil microbes, and upon their formation depends the power of the plants to assimilate free nitrogen of the air. Here the agreement ceases. There are about as many different opinions in regard to the way in which this nitrogen accumulation takes place as there have been investigators of the subject. However it may be, it is

evidently a step in the process of nitrification, in that nitrogen is fixed in a form available to the plant. If, indeed, nitrates are neither produced by the organisms before this absorption takes place, nor within the plant by the action of the cells, it is certainly converted into a nitrifiable compound. It is only from a study of the results of the life action of these micro-organisms that the important role which they play in the many changes taking place in nature has been discovered.

THE EXHAUSTION OF THE COAL SUPPLY.

F. P. VENABLE.

Bodies of scientific men, as the British Association for the Advancement of Science, and various public prints have for some time been discussing the problem of the earth's coal supply and its probable exhaustion. There is a growing uneasiness on the part of the public that the end of our supply of coal is in sight and that we are in danger of running short of fuel. If the agitation of the question would correct the present enormous waste of fuel and lead to proper economy in its use, the gain would be great. The vast waste in coke ovens, the loss in crude furnaces, in imperfect engines and wretched heating appliances is enough to make any thoughtful man stand aghast. For instance, a high authority tells us that the loss in our heating stoves, grates etc., is 80 or 90 per cent, that is, one ton of coal should last us nine or ten times as long as it does now or do that much more work. A family now

using ten tons of coal for heating purposes during the winter could get along very nicely with one ton if the heating arrangements were perfected. Any one who has watched, on a still day, the long lines of smoke left by passing trains or the black trails stretching for miles behind ocean steamers can realize our prodigal waste of nature's generous gift. Still I do not think there is much reason for the dread that we are hastening to a time when the coal question will lead to a new struggle for existence, a painful illustration of the principle styled "the survival of the fittest." Many estimates of the coal supply and its probable rate of exhaustion have been given. These are based on very imperfect data and vary greatly but they all agree in giving us a respite of from one to two centuries. Taking these estimates as approximately correct and agreeing to the assumption that the use will increase at the rapid rate of the past quarter of a century, does not a greater danger threaten than the comparatively slight one of being forced to eat our food raw and winter in the tropics?

Geologists tell us that these coal deposits were laid away at a time when the proportion of carbon dioxide in the air was much greater than it is now. These masses of coal represent carbon dioxide decomposed and so made available by plant life and then stored away. We dig it up and burn it back to the original form, restoring the carbon dioxide to the air. These processes of decomposition and reoxidation go on side by side at present and Saussure has supposed a sort of equilibrium between the forces removing the carbon dioxide from the atmosphere, such as the growth of plants, the washing of rain etc., and those restoring it, as the breathing of animals, combustion of organic matter

and decay. That such an equilibrium exists is not above question. The changes in the amount of carbon dioxide would be so slight from year to year, however, and accurate analytical methods are so recent an acquisition that there is no experimental proof to settle the question. Still, it is clear that if the present proportion of carbon dioxide in the atmosphere is dependent upon a sort of equilibrium between, in the main, the formation of carbon dioxide by combustion and its removal by the growth of plants, this balance cannot be kept up if we enormously increase combustion, at the same time cutting down our forests and so limiting plant growth. The removal of this prejudicial body from the air by the formation of earthy carbonates is too slow to materially affect the result. This means then that the total amount of carbon dioxide in the air must increase and of course its ratio to the oxygen also. It is well known that this ratio does not bear much increase before the danger line is reached.

One of the calculations of the present total amount of carbon dioxide in the air, or carbonic acid, as it is commonly called, places it at some four billion tons. Now taking one of the estimates (Mr. Wister's) of the consumption of coal for one hundred years, namely, 840,000,000,000 tons. we find this is equivalent to about 3,000 billion tons of carbon dioxide. This would give 30 billion tons a year, or seven and a half times the present estimate of the total amount in the air. This amount added to that breathed out by the increasing population of the earth makes it manifest that, before the hundred years are out, we will be in the serious danger of asphyxiation.

Though the above estimates may be somewhat beyond the mark, and, of course, they are offered as ap-

proximations only, one cannot help thinking that two of the great problems of the immediate future will be, devising less wasteful methods for using our fuel and freeing the air from the impurities we so recklessly pour into it.

As to the question of our supply of fuel, the great strides in the knowledge and use of electricity leave little doubt that it will furnish the light, heat and motive power of the future. We will not have to rely upon the etheric force of Keely or others. Every torrent, every waterfall, the motion of the tides, the quiet flow of the rivers, reservoirs of pent-up rainfall, all will be called into requisition to generate for us this force, so beneficent when tamed. Who would have believed a few years ago that it would so soon have attained its present position as motive and lighting power? It is already usurping the place of fuel in extracting the metals from their ores and we have scarcely entered upon the era of its use in the manufactures.

If, however, we must have fuel we need not seek very far for inventions which might supply our needs. It is not conceivable that we shall go on for another hundred years with the inconvenient and wasteful use of fuel in the solid form, any more than we would now be willing to return to the torch and tallow dip of our fathers as a source of light. Gaseous fuel will be the only form marketable in the next century and the sooner we come to this the better. The advantages in the use of gas for heating and industrial purposes have already been experienced by those dwelling in the natural gas region and they are loath to give it up.

The gaseous fuel of the future will consist mainly of hydrogen and carbon monoxide. The first we can easily obtain by decomposing water by means of electricity

and it is only a question of cost that interferes with its present use. The second constituent, carbon monoxide, can be prepared by the same agency from the carbon dioxide or carbonic acid, of which we have been speaking and, if the demand justified it, the methods of production for both of these substances could doubtless be so improved and cheapened as to become entirely practicable.

We must bear in mind that there is no destruction of matter possible on the face of the globe, and our use of the coal means only that we change it into some not immediately useful form from which, as we have just seen, it is possible to recover it, thus bringing it into use again. In this we would be but imitating nature in her cycle of changes. Man dies, his body decays and its constituent materials come into general circulation once more and are ready to be utilized in the building up of a new man. Men burn a plant, some living growing plant somewhere gathers together the materials thus once used and scattered, and gets them into a shape in which man can use them again.

We have not taken into account the possibility, as shown by repeated experiments, of utilizing the sun's heat and the immense amount of energy scattered by it over the earth's surface. We are told that the total amount of this energy poured out every year upon each acre of the earth's surface is some 800,000 horse-power. As Crookes says, what a waste is here! A flourishing crop grown upon that acre utilizes only some 3,200 horse-power and consequently 786,800 horse-power is lost.

Even a small part of this caught, concentrated, set to work, changed into electricity or stored up against a rainy day when clouds come between us and our

source of energy, would suffice for all man's present needs.

Of course, the coming of a time when water-power and sunshine will be the force-giving, and hence wealth producing conditions, will work many changes among the nations and the advice given by some to such countries as England, which can hope for but little under these new conditions, to pay off their national debts and so relieve posterity from all possible burdens, is not without just foundation.

The outlook is, therefore, not so bad as it seems at first sight and we may get along very comfortably, long after our supplies of natural gas, petroleum, and coal have been exhausted. Still economy should be insisted upon and these grand gifts of nature not squandered.

SULPHUR FROM PYRITE IN NATURE'S LABORATORY.

COLLIER COBB.

An interesting occurrence of native sulphur in York county, South Carolina, came to my notice in connection with the work of the University Summer School of Geology, at King's Mountain, in the summer of 1893, and having visited the place again with the class and made a careful examination in 1894, I deem the occurrence well worthy of note and record. Sulphur crystals have been described by G. H. Williams* from the

*Johns Hopkins Univ. Circular, No. 87, April, 1891.

Mountain View mine, Carroll county, Md., and Weed and Pirsson† have described the occurrence and form of crystals from the Yellowstone National Park; but so far as I am able to learn this peculiar occurrence is unique.

On the Greene place, opposite the home of Mr. E. B. McSwain, near the north-east corner of York county, and about two miles from the King's Mountain battle-field, South Carolina, is a well-marked vein consisting of two bands of iron pyrite about one inch in thickness, with a band of calcareous quartz, from one to three inches in thickness, lying between them. This is the condition of things in the unchanged portion of the vein. Following the vein to the northward and downward, we find the quartz honeycombed by the leeching out of the calcite, and later the interstices are filled with native sulphur,* that portion of the pyrite lying next the quartz having been changed to iron oxide. I was unable to find any dikes in the immediate neighborhood, and though the vein was in a portion of its course folded with the schists composing the country-rock, the folded portions were in most instances entirely unchanged.

†Am. Jour. Sci., xlii, 401, 1871.

JOURNAL

OF THE

Elisha Mitchell Scientific Society

VOLUME XI—PART SECOND

JULY—DECEMBER

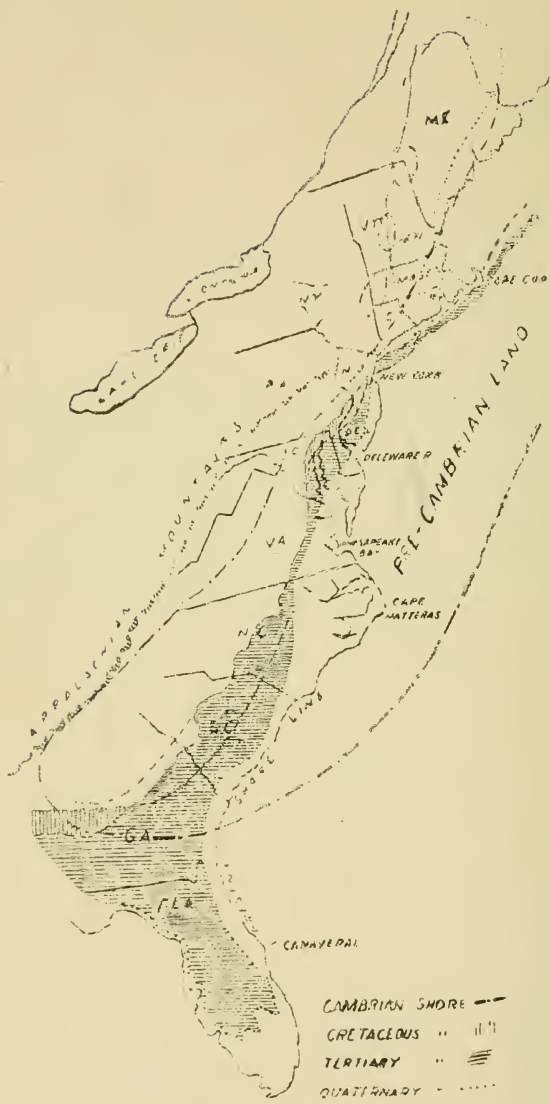
1894

POST OFFICE:
CHAPEL HILL, N. C.

ISSUED FROM THE UNIVERSITY PRESSES,
CHAPEL HILL, N. C.
1894.

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HISTORY OF THE ATLANTIC SHORE LINE.*

HUNTER L. HARRIS.

The history of a shore line consists in an exposition of the changes which have taken place in it; these changes consisting chiefly in its migration across the land surface on which the body of water rests. If this body of water be an ocean or in direct and open communication with an ocean these changes of position may be effected in two possible ways: (1) By an actual depression or elevation of the water surface. (2) By depression or elevation of the land mass along which the shore line occurs.

Without discussing the reasons for such a conclusion we may say that in the great majority of cases the first of these two causes need not be considered as a factor. Usually it is the oscillation of the crust about

* This paper is a thesis prepared in the second course in Geology at Harvard College, and has been furnishrd me by Mr. J. B. Woodworth, the instructor under whose direction the work was done. It is an admirable compilation, and serves as an introduction to the more extended work upon which Mr. Harris had entered at the time of his death.—C. C.

the margin of the ocean that causes the migration. If this be in the nature of an uplift the sea will recede, the shore line successively occupying positions further and further out upon what was formerly sea-bottom. If on the other hand a subsidence of the land surface takes place, the sea will transgress the land and the shore line will successively occupy higher and higher parts of the land slope, that is, further and further inward from its former position.

Slight changes in the position of a coast line may take place in other ways than by bodily movements of the land mass, namely by the deposition of material on the margin of the sea-bottom, thus causing the shore line to recede from the land and by removal of material from the shore, thus causing the sea to transgress the land. These causes are however productive only of comparatively small migrations when acting alone. Evidently we must look upon oscillations of the land mass as the chief cause of change in the position of shore lines.

In order to get at the history of such a shore line as that of the Atlantic of North America, we must know how to read the evidence of its former presence in places other than that now occupied by it. What are these evidences? Probably the most direct, as well as the most exact, evidence is furnished by the actual and characteristic marks left in the form of raised beaches or bench marks. Another evidence is furnished by the position and character of sedimentary deposits,—though the absence of evidence of either kind does not necessarily mean that shore conditions were never present there. While the presence of beach marks furnishes more exact evidence of shore line position in certain cases, the application is not of so wide extent as

the more general evidence of sedimentary deposits, on account of the greater ease with which the former are effaced. The burden of the evidence then lies in the sedimentary deposits of the Atlantic slope, or, more accurately, of that part of North America whose sedimentary deposits can not be referred to some other ocean or water body.

To decide what should be taken as evidence of proximity to shore line we must be familiar with the principles governing the deposition of sediment. Running water is the principal carrier of fragmental materials such as go to make up secondary deposits. These materials vary greatly in coarseness and in composition. Far the greater part, however, is mineral matter, resulting from the decay and disintegration of the rocks of the land, and the fragments which compose it vary from an impalpable powder to the greatest size which can be swept along by water in motion—this latter depending upon the velocity and volume of the current. It is by means of this principle of the carrying power of water that we explain the sorting of those fragments which find their way into moving water. A current of high velocity will transport comparatively large pieces of rock material, until, by decrease of slope or by entrance into some other body of water, its velocity is lessened; then the materials will be deposited, the coarsest first and others in turn as the stream continues to lose velocity. The finest may be deposited a great way out in the ocean, sea or lake, which receives the transporting current.

Since the ocean serves as a receptacle for all the drainage of the land, there is being deposited, within its minor depths and out to a distance of perhaps a hundred miles from the land, all the solid materials

brought into it by streams. And since the ocean provides the gradual retardation of currents which make their way into it, we have a perfect fulfillment of the conditions of water sorting, and, hence, we may declare the general rule that the coarser materials are deposited near the shore and the finer out. Indeed, where we find undoubted marine deposits including fragments of large size such as grit or pebbles, we may reckon with certainty upon the proximity of the sea shore during the time when they were deposited.

So then the presence in any region of such fragmental deposits as may be judged from their nature to be *marine* declare unmistakably the presence there of the ocean at such a date in geological history as our study of these deposits may refer them to. For instance, if we were to find in Western New Jersey marine deposits of Cretaceous age, dipping gently eastward, we should conclude that during the Cretaceous period the Atlantic shore line lay west of that point. How far west it may have stood we must determine by other means, perhaps by actual shore marks, such as a wave cut bench, or a series of beach gravels or sand dunes. Or else from the coarseness of the sediments near their inner border we may conclude that they mark the actual shore line of that period.

Other processes of reasoning are often brought to bear which cannot be dwelt upon within the narrow limits of this paper. We should remember always that such evidences as have been mentioned do not necessarily indicate the greatest amount of encroachment of the sea within any given period, for deposits made further inland may have been removed by the general erosion of the surface: so also shore marks are comparatively seldom left as enduring monuments, and their

absence may be no evidence of the absence of shore conditions.

Of the relative position of land and water (and consequently of the shore-lines) of pre-Cambrian times we know almost nothing. Those changes, which we call metamorphism, have progressed so far, by virtue of the great age of these sediments and their position at the bottom of the stratified series, that it is extremely difficult to read in them the conditions under which they were deposited. We are quite sure that there existed, at the beginning of Cambrian times, a land area, made up of pre-Cambrian sediments, lying somewhere along the Atlantic coast region of North America. A series of very old, highly altered and disturbed sediments now exist as a land area forming an almost continuous belt between the Appalachian mountain system and the present Atlantic border from Canada southward to Georgia. This area, which is in the main supposed to be pre-Cambrian in age, is plainly shown by its structure to have been once involved in a series of complicated mountain building movements, and was in fact part of a great mountain system. Where this land once rose to mountain heights it is now a low, gently sloping and undulating surface made up of hills of gently rounded outline, all rising to about the same height and having in the distance the appearance of a flat country. That is to say it has so long been subjected to the forces of denudation that the mountain ridges which once existed have washed away and finally disappeared, leaving a land surface of low relief and weak topography. What then became of all the material thus removed? It found its way into the borders of the adjoining ocean and was laid down as sediments, and so to the east, south and west of this pre-Cambrian area

lie now upon its edges where they were deposited, the later sediments of the stratified series.

Having found out something of the position of the land of the Atlantic coast region at the initiation of the Cambrian period, we may begin to formulate our knowledge of the shore-line history from that date.

First let us observe that the evidence of former shore-lines given by actual marks of the shore itself is of such a transitory nature that we must not expect to find such evidence in the older rocks. While they may retain a perfectly characteristic form through the Quaternary period or even longer, the chances of their preservation from earlier times becomes less and less as we go back into the geological past. In the Cambrian then we are forced to reason almost entirely from the nature of the sediments, that is, their texture, and composition, and their position with respect to the source of the materials forming them.

There are very few undoubted Cambrian rocks in North America which can with any degree of certainty be ascribed to the Atlantic field of deposition. In the Cambrian Correlation Papers of C. D. Walcott, a series of rocks of Cambrian age, including slates, quartzites, conglomerates and limestones, are located and briefly described under the general name of the Atlantic coast province. These areas are rather small and discontinuous, and extend in a general southwesterly direction from the southern coast of Labrador, across Newfoundland, Nova Scotia, and ending in eastern Massachusetts. The age of each district has been determined by fossils which occur, however, only in restricted zones within the formation. The other members are often classed as Cambrian only on conjecture: hence arises considerable difficulty in interpreting the conditions of

deposition. This difficulty is increased by the removal of the greater part of these rocks by erosion, leaving widely separated patches which can scarcely be placed in any reasonable relation with each other. Usually, however, the series lie upon the eroded surfaces of pre-Cambrian rocks, Laurentian and Algonkian, and often show basal conglomerates formed from those rocks. In such cases the materials seem to have been brought from the west or northwest, and from no great distance. These areas lying about the Gulf of St. Lawrence seem to show by the gradual change in the character of the sediment from basal conglomerate to limestones formed at a moderate depth, that the sea transgressed the Algonkian land westward, allowing the accumulation thereon of the Cambrian deposits, first in shallow bays and afterward in gradually deepening water.

Regarding the Cambrian slates and quartzites of eastern Massachusetts, Prof. W. O. Crosby says; "In general the quartzite is more and the slate less abundant northwestward, indicating that the ancient shore line along which these slates were deposited lay in that direction, and originally the Primordial strata were probably spread continuously over all the region to the southwest of that line." Also, "It is very clear that the quartzite, north and west of the Boston basin, is the source of the quartzite pebbles which play such a prominent part in the composition of the conglomerate, especially in the central and northwestern sections of the basin."

Of the Cambrian section of Bristol county, Massachusetts, Prof. N. S. Shaler says: "The frequent return of conglomerate layers and the coarseness of the pebbles show that during most of the time when the beds were accumulating the region was near shore;

so too the large amount of sandy matter even in the slates affords a presumption that the region was not remote from the coast line. The rocks from which the pebbles were taken were mainly identifiable in the western portion of the field above described. ”

The general inference is then that during a large part of Cambrian time the shore line was in a general way coincident with the present shore-line from Massachusetts northward; that a gradual subsidence of parts of the coast region ensued by which the ocean transgressed the land, accumulating, as it moved inward, a sheet of coarse deposits which were in turn covered by fine argillaceous and calcareous sediments forming slate and limestone. These seem to have been formed in a sheltered sea, hence the opinion is that the land barriers existed somewhere to the *east*. During this inward march of the shore-line there must have been many partial returns to its former position but the general result was an inward extension, amounting in some places to fifty, and in other places to one hundred miles, from its present position.

When we attempt to reckon upon the southward extension of the Cambrian shore-line we are entirely at a loss, for, in the first place, we have no known Cambrian deposits south of New England which can be clearly ascribed to the Atlantic field of deposition. Apparently the Cambrian, as well as the whole of the Paleozoic rocks are entirely missing from the southern Atlantic province. This has led to the belief, which is supported only by negative evidence, however, that during the whole of the Paleozoic era the eastern extension of the continent was much greater than it is now. There is really little doubt that this was the case, and the evidence of land barriers lying to the

east of the New England section during Cambrian times, leads to a conjecture which may here be stated.

A persistent and connected series of Cambrian outcrops lies along the Appalachian mountain system from Alabama to the river St. Lawrence. These are known to have been deposited in the great continental sea which covered the central portion of North America during the whole of Paleozoic time and even later. These Cambrian rocks with the other Paleozoic sediments were involved in the orographic movement which gave rise to the Appalachian mountains. Their present outcrop, however, is adjudged to mark in a general way the eastern border of the continental sea in which they were deposited. To furnish this enormous thickness of Paleozoic sediments a much larger land area must have existed toward the east than now remains. The fact that the denuded surface of much folded pre-Cambrian rocks is seen now to disappear eastward under the present continental shelf, in some measure bears out this idea.

The conjecture now follows, that the Cambrian rocks of New England heretofore described as belonging to the Atlantic coast province form really a part of the Appalachian province; that is, that they were deposited not in the Atlantic, but, along with the not far distant Cambrian rocks of eastern New York in the continental sea. This satisfies the conditions which have been predicated of them, namely, that they were deposited, not in the open ocean, but in a more or less sheltered sea. The elevation of a part of this area in the process of Appalachian mountain building and the subsequent denudation of the whole of New England, reducing it almost to base-level, would account for the existence of the Cambrian rocks only in isolated

patches, while the disturbance of their original stratigraphic position would make it impossible to read any of their history by the stratigraphy.

If this conjecture be true, the "land barriers lying to the east" of New England would be but a part of the broad pre-Cambrian land strip which extended from some part of the North Atlantic in a southwesterly direction almost to the present shores of the Gulf of Mexico. In such case all ideas of the Atlantic shore line previous to the Triassic period are involved in the statement that it existed *at some distance east of its present position*.

Taking up the thread of the history at the beginning of Mesozoic time we find a series of elongated basin deposits of Triassic (Rhaetic?) date consisting chiefly of red sandstones and conglomerates. These rocks form a long train of detached areas stretching from central Massachusetts southwestward to South Carolina. They lie unconformably upon the denuded surface of the pre-Cambrian crystallines, and appear to have accumulated either in shallow inland seas or in sheltered embayments of the ocean. All of them are separated from the present ocean by older rocks, except that of Connecticut, which itself communicates with it only by a narrow neck.

We have, then, in Triassic times very little evidence of the position of the Atlantic shore-line itself. If the Triassic rocks of Connecticut and New Jersey were, as has been thought, deposited in embayed portions of the ocean waters, or fronting the open sea, then we must have had a coming in of the shore-line by submergence of the greater part of the pre-Cambrian land area, by which the Triassic sediments accumulated even upon the edges of the Paleozoic rocks of the conti-

mental province. Such a submergence must have brought the ocean to the very foot of the Appalachian mountains which had received their initial uplift just before the beginning of Triassic time. But, if on the other hand, the deposits were made in lagoon-like bays of inland waters, the ocean shore-line may still have stood as far out as at present, or farther. The evidence is that those areas south of the New Jersey area at least, were accumulated in inland seas. If such was the case — and it is the most probable theory — the Triassic ocean extended inland in a great bay with its center somewhere near the mouth of the Hudson River and its shore-line reaching to the base of the Appalachians in western New Jersey and eastern Pennsylvania whence it swung gradually southward to somewhere near the position of the present shore-line.

The conditions of depositions of these sediments have, however, always been difficult to reconstruct. No solution has ever been offered which proved generally satisfactory. The Connecticut basin seems to represent the estuarine phase of a river which was the ancestor of the Connecticut. From analogy, I would offer as an explanation of the elongated similar basins to the southwest that they also represent drowned portions of consequent rivers which may be reasonably supposed to have existed at so short a time after the folding of the crust which formed the Appalachian system. The character of the deposits would accord well with this supposition.

Following the Triassic period of deposition came an emergence causing a retreat of that part of the shore-line south of New England, by which it assumed a position coinciding with the present shore in Long

Island Sound, but gradually departing therefrom toward the south. In Maryland the departure amounts to one hundred miles inland from the present coast and it continues at about that distance to Georgia, where it swings rapidly westward and northward forming the Mississippi embayment of the Cretaceous ocean.

The extensive denudation, which had been long going on over the permanent land area, now extended over those Triassic rocks which were above sea level, and, by the beginning of Cretaceous time, this area was reduced to surface of low relief, much as it appears today, but somewhat nearer base-level. Of the conditions existing during Jurassic time we know nothing since we have no distinctly Jurassic rocks in this province. But of Cretaceous deposition we have a good record in at least two formations whose inland extension is marked by the Cretaceous shore-line already described.

A study of the earlier of these two formations by W. J. McGee shows that, after the base-levelling of the ancient land area, which was achieved just before Cretaceous times, a shoreward tilting of the area took place by which the streams were revived to such a degree that they rapidly sank into deep narrow valleys. A submergence then caused the sea to invade these estuaries, the coast assuming in general the position which marks probably the greatest transgression during Cretaceous time. Then followed the accumulation of the Potomac sediments which, with their equivalents, extend from New Jersey southward, certainly as far as North Carolina, and probably as far as the Mississippi embayment. A period of emergences and retreat of shore-line then intervened before the deposition of the glauconite beds of later Cretaceous which are seen to

overlie the Potomac. During *later* Cretaceous then the shore line returned nearly to its former position. Close study of the different members of each of these formations would probably reveal signs of shore migrations of comparatively small magnitude besides the sweeping changes herein mentioned. Moreover it is not definitely made out that the inner border of existing Cretaceous deposits is the limit of encroachments of the sea in Cretaceous time. Great denudation, going on in Tertiary time, caused a second base-level to spread over a considerable part of the ancient land area which had been uplifted at the close of the Triassic; and it is to be supposed that much of the denudation took place in the relatively soft Cretaceous beds, by which large areas may have been entirely removed.

Coming now to the Tertiary, we find that while there were undoubtedly many oscillations of level during this period, the principal Tertiary shore-line corresponds closely to that of the Cretaceous from their most northerly occurrence (off Cape Cod) as far south as Virginia. Between these points the two border lines are never more than twenty miles apart. In Southern Virginia, North Carolina, South Carolina, and part of Georgia, the Tertiary border overlays that of the Cretaceous; but from Georgia northwestward into the Mississippi embayment, the Tertiary lies further out, allowing an exposure of the Cretaceous beds in a strip perhaps fifty miles wide.

In the Tertiary of the Atlantic coast province, Eocene, Miocene, and probably Pliocene, sediments occur, though in the case of one or more formations it is difficult to discriminate between Miocene and Pliocene. Hence the term Neocene is often used to describe the Lafayette (Appomattox, Orange Sand) formation of the

middle and southern Atlantic, which has been carefully studied by Mr. McGee. There is usually more or less unconformity between the three or more formations of Tertiary, and often they are not continuous over the whole Tertiary field, but thin out and disappear from some portions while they reach great height and thickness elsewhere. It is difficult to say more than there were at least three migrations of the Tertiary coast-line caused by uplift and subsidence which took place rather unevenly but never causing any considerable transgression over the border line already described.

It is reasonable to expect that the characteristic forms caused by the persistence of shore conditions at certain levels would furnish evidence in the case of such recent deposits as the Tertiary, and doubtless they would if sufficient study had been made even of these terraces, shore cliffs and raised beaches which are known to exist. Such shore marks would enter very prominently into the investigation of the Quarternary shore-line to which our attention must now be directed.

It should be remembered that there has been a successive addition of essential land surface along the Atlantic slope from Cape Cod southward through all the geological time from Triassic down to Quaternary, and a consequent recession of the shore-line eastward. From Cape Cod northward, however, the reverse has to some measure been true, that is, there has been an excess of subsidence over the constructive processes by which all the deposits from the beginning of the Mesozoic to the Quarternary, if formed at all, are now buried beneath the sea.

The most marked feature of Quarternary time was the great ice invasion. A prodigious accumulation of ice in the northern half of the continent was accompan-

ied by a spreading out of its mass on all sides so that it extended southward far into temperate latitudes, reaching at its greatest extension the middle courses of the Mississippi River. On the Atlantic coast of New England the glacial covering spread into the sea and probably floated off as icebergs. As a result of the abrasion and transport of rock material by the ice, the glacial field is covered with deposits of irregular distribution and possessing the peculiar characters by which they are readily distinguished from ordinary aqueous sediments. During the formation of some of these glacial heaps, the land along the North Atlantic coast must have stood somewhat higher than at present. Some of these deposits, which were evidently made upon the land, now lie as small wasting islands off the present shores. Indeed it has been claimed that the central part of the glacial field must have stood much higher at the beginning of the glacial period than now, the difference amounting to thousands of feet in the region just south of Hudson's bay, which was supposed to have been the glacial centre. This has been supposed a necessary condition to account for the accumulations of snow and ice in such enormous quantities, and its descent into lower latitudes. There is evidence of such a condition in Europe in the fiorded Scandinavian coast, as has been pointed out by Dana, and the submerged valleys extending out from the Hudson and other rivers may be cited as an American evidence of a similar sort. But we have much clearer evidence of *submergence* during a later part of the glacial period, which amounted to only a few feet at New York City but increased northward, — reaching 200 to 225 feet off the coast of Maine, 500 to 600 feet at Montreal and 1000 feet on the coast of Labrador.

These approximate figures are taken from careful measurements by various observers of the heights of certain shore cliffs and marine deposits shown to be of Quarternary age. I have omitted measurements of various points between, and have given in the place of exact figures a sort of general average of the observations of several persons, arranged in such a way as to show the gradual increase in the amount of submergence going northward.

It is difficult to reconcile the views held by various geologists of the amount of subsidence which took place at several points along the New England coast and northward. The differences depend on different criteria used in the discrimination of shore-lines, difference in opportunity for and general incompleteness of observation, etc. The consensus of opinion, however, as regards the Atlantic shore-line is about as I have represented it. The result of such a subsidence must have been the submergence of parts of the Maine coast, parts of Nova Scotia, Newfoundland and Labrador, and of a large area extending up the St. Lawrence River to the Great Lakes.

Of the middle and southern Atlantic coast little has been done in discriminating and tracing the many shore-line terraces of Quarternary age which undoubtedly exist as distinct features. Some mapping of the Quarternary deposits has however been made. Of these, one formation has been studied by McGee and named the "Columbia" loam. It belongs especially to the middle Atlantic slope and is older than the moraine deposits of the glacial epoch. It is both fluvial and marine and is scarcely observed southward from North Carolina, where its inner border approaches the present coast. It represents a brief

glacial submergence amounting to 400 feet in the northern part of the field (New Jersey) and almost nothing at its southern limit.

Other Quarternary formations occur in the southern field, of which the shore-line limit lies 10 to 50 miles inland, from South Carolina to Florida. Here the Quarternary forms one third of the peninsula (the southern end) and thence the division line swings along the Gulf coast where it marks off a border formation almost equal in width to the similar strip along the Atlantic states.

Far the largest area of land surface which has been added to the Atlantic border is seen to to be of Tertiary age. On the inner border of this a narrow strip of Cretaceous and on the outer edge a thin layer of Quarternary sediments, make up, taken with the Tertiary, practically all that the continent has gained; and the area represents the final amount of recession of the Atlantic shore-line during recorded geological time. North of Cape Cod the result of oscillation so far has been on the other side, and the coast-line now probably stands farther in upon the land than at the beginning of recorded time. Here we have lost rather than gained continental area.

The subjoined map attempts to represent the Atlantic shore-line history in the order in which I have attempted to compile it in this paper. The study has necessarily been crude and incomplete in its nature and is offered as an introduction to a more critical and extended study which may be undertaken later on.

REFERENCES:

- LeConte.— *Elements of Geology*. 3d edition.
 Walcott, C. D. — *Cambrian Correlation Papers*; Bulletin 81, U. S. Geol. Survey, (Atlantic coast Province).

Shaler, N. S. — *On the Geology of the Cambrian District of Bristol Co., Mass.* Bull. Mus. Comp. Zool. XVI., pp. 24-26.

Davis, W. M. — *The Geological Dates of Origin of Certain Topographic Forms of the Atlantic Slope of the U. S.* Bull. Geol. Soc. America, II., pp. 548-581.

Shaler, N. S. — *Geology of Mount Desert Island.* 8th An. Rept., U. S. Geological Survey.

□ McGee, W. J. — *Three Formations of the Middle Atlantic Slope.* Am. Jour. Sci. XXXV.

DeGeer, Baron Gerard. — *On Pleistocene Changes of Level in Eastern North America.* Proc. Bost. Soc. Nat. Hist., XXV., 454-477.

AN EXAMINATION INTO THE NATURE OF PALÆOTROCHIS

CHARLES HENRY WHITE.

While Professor Ebenezer Emmons was "Geologist to North Carolina," he discovered a singular form in Montgomery county which he believed to be a fossil. He announced the discovery in 1856, and owing to the low horizon in which he found it, regarded it as the oldest representative of the animal kingdom on the globe, and gave it the name *palæotrochis*; old messenger. At this time he wrote a letter to one of the editors of the American Journal of Science in which he said: "It is evident that the fossil is a coral," and described it as follows: "Form lenticular and circular and similar to a double cone applied base to base; surfaces grooved, grooves somewhat irregular but extended from the apices to the base or edge."¹

In his Report of the Midland Counties of North

1, American Journal of Science, Vol. XXII. 2nd Series, p 390.

Carolina, on plate 14 opposite page xx., he gives a section of the region in which the palæotrochis is found, which is reproduced in Fig. 1. On page 61 of the same is the following descriptive section, enumerated in the ascending order:

1. Talcose slates, passing into silicious slates, and which are often obscurely brecciated. Thickness undetermined.

2. Brecciated conglomerates, 300-400 feet thick, and sometimes porphyrized.

3. Slaty Breccia, associated with hornstone.

4. Granular quartz, sometimes vitreous, and filled with fossils and silicious concretions of the size of almonds; 200-300 feet thick.

5. Slaty quartzite, with a very few fossils, about 50 feet thick.

6. Slate without fossils, 40 feet thick.

7. White quartz, more or less vetrified, filled with fossils and concretions; 700-800 feet thick.

8. Jointed granular quartz, with only a few fossils.

9. Vitrified quartz, without fossils; 30 feet thick.

10. Granular quartz, no fossils, and thickness very great, but not determined.

He says that some of the rock beds in which these forms occur consist almost entirely of them, and are intermixed with almond shaped silicious concretions "which frequently contain the fossil." He speaks of their occurrence from the size of a small pea to two inches in diameter, but by far the greater number belong to one or the other of two sizes; the smaller size represented by Figs. 2-4, and the larger by Figs. 8 and 9. The smaller he calls palæotrochis minor, and in addition to the characters given above, "the apex of the inferior size is excavated, or provided with a small

roundish cavity, with a smooth inside, or sometimes marked by light ridges, which may be accidental; the opposite side is supplied with a rounded knob, from the base of which the radiating grooves begin."¹ In the larger, or palæotrochis major the rounded knob and opposite cavity are absent.

"This fossil is a silicious coralline, and not silicious from petrification. It seems never to have had a calcareous skeleton like most corallines: but, during its existence, to have been entirely composed of the former substance. The animal was gemmiferous—the germs being sometimes cast off, in which case new and independent individuals were produced; on others, the germs adhered to the parent. These start from the circular edge at the base of the cones; their growth produced a change of form which is illustrated in Figs. 2 and 4."²

"The palæotrochis is found at Troy, Montgomery county, at Zion about twelve miles south-west of Troy, where the fossil occurs in the greatest profusion. It has also been noticed on the road from Troy to Birney's bridge."³

Shortly after the description of the palæotrochis was published, Professor James Hall, in a letter to Professor Dana,⁴ suggested that these forms were merely concretions. In 1868, Professor O. C. Marsh in an article on this subject in the American Journal of Science says that he suspected that they were inorganic and an examination of the interior clearly indica-

1. Geological Report of the Midland Counties of North Carolina E. Emmons. p.62.

2. *Ibid* page 63.

3. *Ibid* page 64.

4. American Journal of Science Vol. XLV. p. 218.

ted that they were not corals, and as soon as microscopical sections could be prepared, they were more carefully examined, but no trace of organic structure could be detected, the entire mass being evidently a finely grained quartz. It follows therefore, he says, that this name should in the future be dropped from the genera of fossils. He says further: "Admitting the inorganic nature of these remarkable forms, their origin becomes an interesting question and it is certainly not easy to give a satisfactory explanation of it," but, that it seems to have some analogy with cone-in-cone structure which is probably due to the action of pressure on concretionary structure when forming. In some respects the two are quite distinct, but evidence of pressure is clearly to be seen in both. ¹

With this the matter seems to have been dropped except a general unrest among scientists, into whose hands the specimens came, that the results obtained should not be final.

The late Professor W. C. Kerr, State Geologist, made a collection of these specimens with a view to making an examination of them but did not live to do the work. That the subject might be further investigated, Professor J. A. Holmes, State Geologist, visited the region and collected a large number of specimens. For the same reason, Professor Collier Cobb, at whose suggestion and under whose direction I make this examination, obtained an original specimen collected by Professor Emmons, from the Massachusetts Institute of Technology.

With this brief history of the palæotrochis, let us examine its character, mode of occurrence, etc.

1. American Journal of Science, Vol. XLV. p. 219.

The specimens I have used are those collected by Professor Emmons and Professor Holmes, referred to above.

The rock mass in which the specimens occur is granular quartz of a dark color and splits roughly along apparent planes of bedding. The weathered surface of the rock is very rough, consisting of the protruding fossil-like forms and cavities out of which they have weathered, interspersed with more or less even patches of weathering concretions.

These protruding forms are composed of quartz of a light gray color, sometimes brown from oxides of iron. Around each of these forms there is a ring of softer grayish white material, which in many cases has weathered below the general surface of the rock, leaving the forms standing up apparently in little cups. The concretions in weathering are also grayish white and are circular in section, showing concentric structure about very small nuclei. The fossil-like forms of the palæotrochis are larger than the concretions. I counted in an average specimen, twenty of the palæotrochis exposed in an area of nine square inches, which averaged about three-eighths of an inch in diameter, never varying much from that size. The concretions were somewhat more numerous and considerably smaller. The palæotrochis is not distributed evenly through the rock nor does it occur in definite planes of stratification. The individuals are turned in no definite position with respect to each other, but with very rare exceptions one apex or the other of the double cones rests on bedding planes or on planes parallel to these—not with the axis perpendicular to the plane but inclined at a varying angle depending upon the flatness of the form. In other words, their general position is

that which they would assume if left under the influence of gravity to collect under water. Figure 10 is a section at right angles to the bedding planes showing their mode of occurrence.

The rock mass clearly shows evidence of considerable pressure at right angles to the bedding planes. This is not only shown by the mass, but often by individual specimens as shown in Fig. 11, which, lying in the position it would naturally assume, received the pressure from above, giving it its present form with the vertical plane of fracture which has since been filled. Owing to the shape and position of the specimen, the pressure would be unequally distributed, fracturing it in the direction shown for the obvious reason that the greatest stress was in that plane. Lines of fracture are also found in microscopic sections of specimens which do not show it externally, Fig. 12.

In form, isolated specimens and those exposed on the weathered surface of the rock, answer to the description of Emmons, given above (pages 50, 51, and 52; also see figures 2-7). But when the weathered surface is broken away and a fresh surface is exposed, these forms are enveloped in a gray, translucent, radial fibrous mineral, which under the microscope proves to be an impure chalcedony. This, as we would expect, weathers gray-white on exposure¹ and is washed away faster than the surrounding rock. The interior, or palæotrochis proper, I find is granular quartz as did Marsh. The small concretions prove to be chalcedony throughout. There is a definite line of separation between the chalcedonic formation and both the surrounding rock on the outside and the enclosed palæotrochis.

1. See page 54; also Text Book of Geology. A. Geike—Third Edition. 1893, p. 69.

The concretions are also distinct from the rock mass. Figure 13, taken from a microscopic section, roughly illustrates these points.

Having the general characters of palæotrochis before us, let us now compare it with the forms that it has been thought to resemble and examine more carefully the more minute details.

(1) Is it a concretion? "There is a general tendency in matter, when solidifying to concrete around centres. These centres may be determined (1) by foreign substances which act as nuclei, or (2) by the circumstances of solidification, which according to a general law, favor a commencement of the process at certain points in the mass, assumed at the time. As the solidifying condition is just being reached, instead of the whole simultaneously concreting, the process generally begins at points through the mass; and these points are the centres of concretions into which the mass solidifies.

"The concretions in the same mass are usually nearly of equal size; hence the points at which solidification in any special case begins are usually nearly equidistant.

"In a concretionary mass, the drying of the exterior, by absorption around, may lead to its concreting first. It then forms a shell with a wet unsolidified interior. The interior may then dry, contract, and become cracked; or, it may undergo no solidification, and remain as loose earth; or, it may solidify by the concreting process, forming a ball within a shell, with loose earth between."¹

If the forms we are considering were even spherical,

1. Dana's Manual of Geology, page 628.

the most general concretionary form, we should still have no difficulty in deciding that they do not belong to the last class, since the interior is a compact mass of semi-crystalline quartz, often showing the layers in which it was laid down by the ordinary process of deposition. (Fig. 14.) From what has been said of their distribution (p. 54), they could not belong to the second class. The chalcedonic envelope is distinctly concretionary, and regarding the palæotrochis as a nucleus, they *can* belong to the first class. But the palæotrochis itself is no ordinary concretion, which Marsh admits and tries to find some analogy between it and cone-in-cone structure.

(2) Is it stylolites or cone-in-cone? "Stylolites are cylindrical or columnar bodies varying in length up to more than four, and in diameter up to two or more inches. The sides are longitudinally striated or grooved. Each column usually with a conical or rounded cap of clay, beneath which a shell or other organism may frequently be detected, is placed at right angles to the bedding of the limestones, or calcareous shales through which it passes, and consists of the same material. This structure has been referred by Professor Marsh to the difference between the resistance offered by the column under the shell, and by the surrounding matrix to superincumbent pressure. The striated surface in this view is a case of 'slicken-slides.'"¹

It is true that the palæotrochis shows signs of pressure, but, as already pointed out (p.55), the pressure had a tendency to deform the structure and obliterate the grooves or striae instead of forming or constructing them, while the layers of deposit of which the forms

1. Text Book of Geology. A Geikie. 3d. Edition, 1893, p. 316.

are composed, show that there was no pressure when forming. (p. 56, also Fig.14.) Neither are they in the slightest degree similar in form.

“Undoubtedly few of the structures classed under the general head of concretions are more curious than cone-in-cone. The name is descriptive, the structure consisting of corrugated or crenulated conical layers, one within another, and in the more complex specimens it is seen that thin layers of the rock, a calcareous and sideritic clay, is composed of the closely crowded nests of cones, the axes of the cones being transverse to the bedding planes. The height of the cones measures the thickness of the layers, which is commonly one to four inches. It seems necessary to suppose that during the compression of the layers of clay by vertical pressure it is divided by an indefinite series of conical gliding surfaces, which are corrugated by the intermittent character of the movement.”¹

“Clay iron stones sometimes exhibit the regular structure known as cone-in-cone, in which case the seam has a tendency to divide into cones, the bases of which are towards the top and bottom of the bed, while their apices are directed towards the center.”²

By comparing the character and mode of occurrence of palæotrochis with cone-in-cone, it is seen that there is no similarity between them, but the quotations are given in full to show that no inorganic form has yet been described which explains the origin of palæotrochis.

The palæotrochis is not two cones applied base to base, that simply roughly suggests the general form, and its failure to conform, even approximately, to a

1. Dynamical and Structural Geol., W. O. Crosby, p. 278.

2. Ore deposits, J. A. Philips. p. 165.

geometric figure and its freedom from rigidity in its appearance, either in form or markings, suggests that it is not of inorganic origin. And yet the persistence in conforming to a general outline, in the radial groovings, and the rounded knob at one apex with the smooth cavity at the other makes the conclusion irresistible that it is not "accidental," that they were all formed under like conditions and in accordance with certain laws, and no mode of crystallization or wholly inorganic arrangement can be conceived that will supply the conditions or suggest the laws capable of imitating these forms. The rounded knob and the cavity opposite are very striking. I have examined many isolated specimens and without exception the knob and cavity are present. Those exposed on the surface of the rock, as has been pointed out, generally show one of the apices, and of those I have examined—upwards of 300 in all—not one failed to present either a knob or a cavity,¹ with the exception of not more than four whose apices had been so crushed by pressure that these characters had been destroyed, or the knob simply broken off as in figure 11. I have never yet found one that had a knob at each apex or a cavity at each apex. These two markings seem to be as persistent and as characteristic as the two valves of a brachiopod. The cavity has the exact appearance of the socket of a ball and socket joint. The inner surface appears perfectly smooth under a magnifying glass and vividly suggests that it has been the seat of an organ or of an organism.

(3) It has been shown so far that the palæotrochis

1. This statement applies only to those which present an apex and not to those rare exceptions that do not present either apex.

is not similar to any concretion or class of concretions heretofore described and that it has no analogy to cone-in-cone or stylolites. Let us now examine the evidence by which Professor Marsh came to the conclusion that it is not a coral and see if he was justified in that conclusion.

His conclusion, given on page 52 of this paper, is not drawn from the form or external markings, but when he examined the interior with a microscope and found no organic structure he deemed the evidence sufficient and concluded that in the future this name should be dropped from the genera of fossils. If he had found organic structure of course the proof would have been direct and positive, but the absence of organic structure is by no means a proof that it is of inorganic origin, for Nicholson and Lydekker say, in speaking of replacement by silica, the following: "In a large number of cases of silicification, the minute *structure* of the fossil which has been subjected to this change is found to have been more or less injuriously affected, and may be altogether destroyed even though the *form* of the fossil be perfectly preserved. This is the rule where the silicification has been secondary, and has taken place at some period long posterior to the original entombment of the fossil in the enveloping rock."¹

Therefore it appears that Marsh's determination can not be relied upon.

(4) Was Professor Emmons justified in his statement that it is a coral? It is true the general form, the radiate striae, or grooves, and what he took to be

1. Manual of Palæontology—Nicholson and Lydekker. Vol. 1. p. 7.

the method of reproduction as described above (p. 52) might have seemed to him more suggestive of the coral than of any known form, organic or inorganic, yet the proof is not positive and I can find no just ground for his position.¹

Admitting the organic origin of palæotrochis, how could it have been preserved? Considering its distribution through the rock mass and the position assumed by the individuals, with the material in which they are imbedded, the explanation is possible by different methods. The first that occurs to me, and which is offered merely as a suggestion is this: The individuals dropped to the sea floor and were imbedded in ooze. This ooze being largely calcareous but containing a considerable amount of silica on beginning to solidify would have formed in it, silicious concretions, just as they are found in the chalk beds of England. Their origin is explained as follows by LeConte: "Nodular concretions seem to occur whenever any substance is diffused in small quantities through a mass of entirely different material. Flint nodules in chalk. Carbonate of lime modules in sandstone, &c."²

As concretions start around nuclei which are generally of a different material from the concreting substance, and are particularly favored by decaying organic matter, it is quite natural to expect these bodies of organic matter to be encased with silica at the same

1. I have found several specimens that answer to Professor Emmons's description of the process by which they are reproduced, and at apparently different stages of the process. One of the best, which was not in Emmons's collection, I have shown in Fig. 15. This answers better to his description than his own figures, 2 and 4.

2. LeConte's Elements of Geology, p. 188.

time the small spherical concretions are being formed about minute nuclei. Chalcedony often encloses organic forms and so perfectly that the colors of the plants thus encased are preserved.¹ After a great lapse of time let all the calcareous matter of the deposit be replaced by silica, and then follow a period of pressure and uplift and you have the form as it occurs to-day.

That solutions pass through chalcedonic envelopes is shown in water geodes and in geodes containing bitumen.² In this view we would expect the cast of silica in the shell of chalcedony to be purer than that which surrounds these forms. This is observed to be the case with palæotrochis. (p. 54). And from the rule of replacement by silica (pp. 60, 61) we would be surprised to find internal organic structure.

It is not the purpose of this paper to assign these forms to any class or order, not even to show whether they are animal or vegetable. But in passing we may note certain classes of organisms, to one of which it may be referred at some future time.

(1) It might have been a calcareous sponge whose spicules were destroyed by replacement. Though as no spicules have yet been found, it can not be put down as a sponge.

Figure 16 represents a sponge similar in form to the palæotrochis.³

(2) It may belong to the class hydrozoa.

1. Transactions of the Geological Society, Vol. II. First Series. p. 510.

□2. Dynamical and Structural Geology. W. O. Crosby, p. 275.

3. Ward's Catalogue. p. 205. For description see Transactions of the Geological Society. Vol. 1. p. 337.

(3) It may be an organ of some animal. The form represented in figure 17 is a "cast of what Nathorst considers to be the radial canals of a species of a craspedot Medusa, belonging to the family *Æquoridae*." ¹

(4) They may prove to be of vegetable origin; another variation of the many and striking forms assumed by sea plants.

From the peculiar nature of the knob and cavity, I offer as a bare suggestion that in their original growth they were probably joined together as in Fig. 18.

These are mere suggestions to show that the palæotrochis is not wholly unlike all organic forms, though it can not yet be assigned a definite place among organisms.

The purpose of this examination has been to call attention to the work done on the palæotrochis, to investigate the methods by which the results were obtained, and to see if the conclusions reached would stand the test of an examination made in the light of more recent discoveries and by more modern methods.

I claim (1) that neither Emmons, Hall, nor Marsh made that careful and scientific investigation of these forms necessary to justify the conclusions reached, and that these conclusions should not be accepted. And I claim (2) that the weight of evidence in the present state of knowledge indicates that the palæotrochis is of organic origin. The reasons briefly summed up are:

(1) Its distribution in the rock. (p. 54)

1. 10th Annual Report, U. S. Geological Survey, 1888-'89, Plate op. p. 676.

- (2) Positions assumed by the individuals. (pp. 54, 55).
- (3) Their conformity in shape to a general type as persistently as that of any class of organisms. (pp. 51-58).
- (4) The failure to conceive of any inorganic process by which such forms could be produced. (p. 59).
- (5) That they attract concreting material and are the nuclei of concretions. (pp. 54, 56).
- (6) Their general resemblance to determined organic forms. (pp. 62, 63).
- (7) An apparent method of reproduction, (pp. 52, 61).

It may take years of patient examination to find direct and positive evidence by which the palæotrochis may be referred to its proper place among organisms, and such evidence may never be found, yet I believe the importance of the subject justifies a much more extended and careful examination than it has yet received.

EXPLANATION OF PLATES.

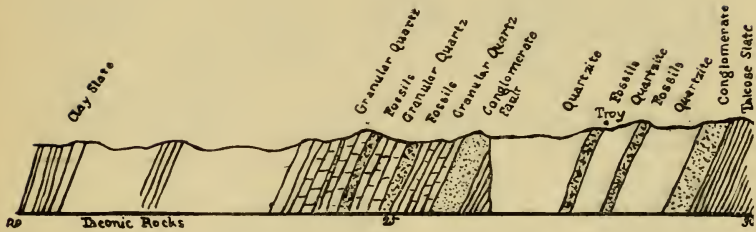


Fig. 1. Section through region of Palæotrochis Beds. After Emmons.

Figs. 2, 3 and 4. *Palæotrochis mtnor.* After Emmons.

Figs. 5, 6, 7. Specimen found by Emmons, in possession of Prof. Collier Cobb.

Figs. 8 and 9. *Palæotrochis major.* After Emmons.

Fig. 10. Showing position of fossils in bed.

Fig. 11. *Palæotrochis* deformed and fractured by pressure.

Fig. 12. Microscopic section showing fracture.

Fig. 13. Microscopic section showing chalcidonic envelope.

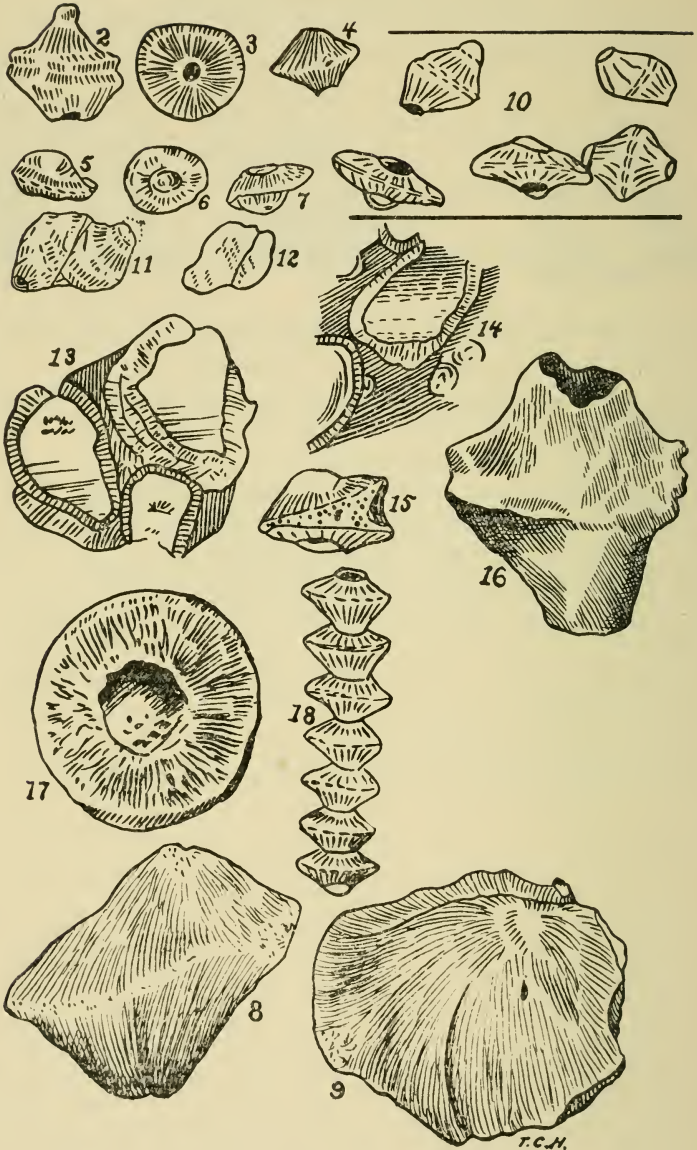
Fig. 14. Polished surface of rock showing layers of deposition in specimen.

Fig. 15. *Palæotrochis* showing what Emmons described as budding.

Fig. 16. Sponge.

Fig. 17. An organ of medusa.

Fig. 13. Suggestion as to possible arrangement of *palæotrochis*.



THE ATOMIC WEIGHTS AND THEIR NATURAL ARRANGEMENT.

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F. P. VENABLE.
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It is proposed in the following paper to emphasize the necessity for the acceptance of oxygen as the standard for the atomic weights, to point out the fact that their absolute determination is not within the bounds of reasonable hope; to show the folly of speculations as to the primal elements in the present state of our knowledge; and to suggest certain changes in the Periodic Arrangement of the elements as given by Mendelejeff.

THE OXYGEN STANDARD.

In 1888 the writer of this paper published in the *JOURNAL OF THE ELISHA MITCHELL SCIENTIFIC SOCIETY*, (Vol. V. 98.) a plea for the adoption of Oxygen as the standard for atomic weights—a return to the very wise and scientific usage of Berzelius. A reprint of this paper was sent to the *London Chemical News* and must have been in the hands of the editor of that journal when there appeared in its pages a paper by Dr. Bohuslav Brauner, of Prag, upon the same subject. The reprint mentioned was published in the *Chemical News* a week or so later. The same standpoint was taken in the two papers and largely the same arguments used. Indeed it seemed almost incredible that the two could have been written entirely independently of one another. These facts were adverted to by Dr. Brauner in a subsequent paper in the *Berliner Beri-*

chte (Ber. deutsch. chem. Ges. XXII. 1175.) when the question was being discussed between Meyer and Seubert, Ostwald and himself.

This was six years ago. The matter has not been much discussed in the mean time. Still the desired result has been partially attained. Many chemists seem to have adopted the oxygen standard and it is made use of in most recent work in this line. Some have spoken of this as only a temporary abandonment of the hydrogen standard. This can be true only in case the chief argument for the oxygen standard ceases to be valid. This argument is, that, in the majority of cases the atomic weight determinations involve combinations with oxygen and hence the use of its atomic weight in calculations. This weight should by all means be fixed and not dependent upon determinations of the ratio to hydrogen or any thing else, to be upset every few years by new and "more accurate" determinations. Only in two cases can hydrogen replace oxygen as the standard. First, in case suitable compounds of the various elements and hydrogen can be obtained. This does not seem very probable. The second case is where absolute accuracy of determination is conceded as impossible and the final atomic weights can be settled upon by some methods of mathematical calculation. Such methods have been suggested but their adoption does not seem probable. It is scarcely necessary to point out that the use of O as 16 or O as 15.96 would make a very marked difference in the cases of elements of high atomic weights—several integers for uranium for instance. Oxygen as 16 must remain the standard for the present and it will be so considered in the remaining portion of this paper and uniformity in this regard is very earnestly to be

pressed upon all who desire the advancement of the science.

HOW FAR IS ACCURATE KNOWLEDGE OF THE ATOMIC WEIGHTS ATTAINABLE?

The atomic weights are generally considered the most important constants in chemistry and yet so imperfectly are they known and so varying the numbers assigned them that it has not been possible so far to settle finally whether they really are constants or variables within narrow limits. The probability, however, is so greatly against this latter view that there are few who are inclined to accept it. As more than three quarters of a century of work has been expended upon them, work engaging the utmost efforts of the masters of the science, as Berzelius, Dumas, Marignac, Stas and many others, it may with perfect justice be asked whether absolute accuracy is attainable.

Some have hoped that the more perfect knowledge of the chemists of the present, the better methods of separation, purification and general manipulation, and the fine balances, would enable them to attain to the desired accuracy. There have been, of course, many improvements but any one who will carefully examine the determinations of Berzelius will find many of them in marvellous agreement with the finest work of late times and when he goes over the list and sees for how many of these atomic weights the work of Berzelius is still relied upon as the best, he will be less boastful of the progress and less hopeful of results from it.

Certainly, if accuracy is to be attained, then the usual method of those who re-calculate these weights, and in fact the only allowable method at present,

namely, that of taking the work of different authors, and critically averaging it, must be rejected, for this would never secure concordant results as they would have to depend upon the judgment of the critic and calculator. All of this back work must be wiped out of existence, except for historical use, and we must begin anew with every conceivable refinement of method and apparatus, perhaps devoting, as has been suggested, some central endowed laboratory to that work and that alone.

Calculations of "probable errors" have given a seeming accuracy to many atomic weight determinations. In this chemists have followed the lead of Stas. It seems to me that this is very misleading, these calculations often being made upon small series in which the possible error, as shown by the variation in individual experiments, is ten times that shown by the calculation. In the proposed new determinations this method of calculation should only be allowed in the case of several hundred closely agreeing determinations.

Of course, it might as well be confessed that absolute accuracy is not to be even hoped for. The best methods and appliances which can be devised or manufactured will always be imperfect and there is besides the personal error of the observer to be allowed for. To what extent shall we demand accuracy, then? Where shall the line be drawn? Is it to be at the first decimal place or the second? It seems useless or hopeless to speak of the third. There can scarcely be said to be an atomic weight at present known correctly to the first decimal place. Take the numerous determinations for oxygen, exceedingly modern and excellently well carried out, and see how they vary between 16.0, 15.9 and 15.8 and look at the original series from

which these results were calculated and see how they are but the means of series with decidedly varying figures—a balancing of errors perhaps. One is induced to think that for many years, at any rate, the highest attainment to be hoped for will be a correct first decimal.

These being the facts, it is but false pedantry in the present state of our knowledge to write these figures beyond the integer in most cases unless the decimal is a large one. In a few cases the first decimal might be used. In no case is the second justifiable. What would be gained by a knowledge of the absolute atomic weight beyond the satisfaction of having secured that much knowledge of the truth? Do these costly labors promise results sufficiently valuable to justify them or are the energies of many of the most skilled chemists misdirected and wasted? Of course no true labor is wasted, but an energy which would accomplish grander results in some other direction is wasted if turned into trivial channels. All will acknowledge that no good to practical chemistry would result from weights known to the second decimal place. If known approximately to the first every requirement of the analytical chemist would be satisfied.

Two things may be gained for science however by such knowledge. First, the question of constancy of weight would be settled, beyond all reasonable doubt, and secondly, data would be obtained for the discovery or confirmation of underlying laws.

Some dim presentiments of such laws were seen when these weights were in their most chaotic state. The vision of them was obscured by the confusion of standards and the disagreement in determinations. As these difficulties were partially removed the way

became clearer for the discovery of the inter-relation of the elements and the dependence of their properties upon their atomic weights. It must be remembered that for several of the elements the atomic weights are unknown and for others are very poorly determined. It is extremely important that these be correctly determined, and work spent upon them is far from wasted, but I must confess that I can not but feel that further efforts to discover the ratio between hydrogen and oxygen are of little value to science and that chemists generally would be more grateful were the same labor devoted to such elements as thorium, cerium, or nickel, and many others.

The question of the variation of the elements in their atomic weights is a very elusive one and scarcely capable of being finally settled by even the most accurate work of the chemist. The supporters of the hypothesis have always a loop-hole of escape in the limits within which these numbers may be supposed to vary. This variation is now narrowed down to the decimal places. As the determinations become more accurate, it is easy for the limit to be moved from one decimal to another and so defy pursuit. Nothing but absolute accuracy, an accuracy shown in every experiment, with all sorts of varied proportions, and not an averaged result, could finally end the discussion. But with a settled standard and the atomic weights known to the first decimal place, the way would be clear for laws dependent upon their inter-relation.

APPROXIMATION TO WHOLE NUMBERS.

Speculations upon the numerical relations existing between the atomic weights began almost with the

first imperfect list of these weights. These took two directions. First the ratios to some common standard or unit as hydrogen, and secondly the relations between the weights of elements of the same group or family. The first subject was looked into simultaneously in the year 1815 by Prout in England and Meinecke in Germany. The second was naturally taken up some years later, the first to suggest numerical regularities being Döbereiner in 1817 and he has been followed by a number of others.

Prout's hypothesis has always attracted the most attention. It may well be divided into two parts: first, an assumption that the atomic weights are all whole multiples of hydrogen. This was afterwards modified so as to read that they were all integral multiples of the half atom of hydrogen. This half atom, or rather body having half the atomic weight, was called pantogen. The second was a deduction from the first assumption. If they were multiples of hydrogen, then they must be composed of hydrogen or of pantogen. Why this should be the case or was at all a necessary deduction no one seems to have attempted to show.

The first assumption has been examined and worked over by many investigators with a view to proving its truth or falsity. If proved true, it would be interesting and useful, but it could never justly be claimed as showing that the elements were formed of hydrogen or the hypothetical pantogen. If we take the list of atomic weights as calculated by Ostwald and select those in regard to which we can feel sure that the weight is approximately correct and if we disregard variations of less than one tenth from the unit, then we find that twenty-three out of thirty-five are integral

multiples of hydrogen. Clarke claims forty-one out of sixty-six but includes such as niobium, didymium, gallium, tungsten, thorium, &c. A little critical examination of his list will easily cut the whole number down to little more than half of the forty claimed. The best that can be said is that about two in three are whole numbers and the remainder run the full range of decimals from .1 to .9 and no halving of the atomic weight can possibly hit upon them. When it is considered that about as many of the elements are whole numbers when hydrogen is taken as 1.0025 as when it is equal to unity, it will be seen how little bearing upon hydrogen as the primal element the facts of integral atomic weights would have.

THE IMPROBABILITY OF HYDROGEN BEING THE PRIMAL ELEMENT.

I hesitate to discuss this question because I scarcely think it is seriously urged but a few thoughts may not be amiss. The supposition of a primal element having as its atomic weight half or any other fraction of the weight of hydrogen is based simply upon the increased number of coincidences of the atomic weights with whole multiples and can have little weight. Such an hypothetical pantogen escapes all serious argument. But against the supposition that hydrogen is the primal element many things may be urged.

In its favor there is little beyond the fact that some two-thirds of the different atoms, so far accurately determined, have approximately integral weights and that, in the table of elements, hydrogen occupies a most anomalous position and refuses to be satisfactorily arranged in any of the groups or periods. If,

however, we are to judge of this matter by ordinary rules, it seems highly improbable that an element of such definite, positively marked characteristics can by any kind of condensation or combination be changed into such markedly opposite bodies as fluorine and sodium or chlorine and potassium. We are coming more and more to regard an element as representing an assemblage of properties. Thus chlorine stands for a form of matter, gaseous and most energetically negative whilst a slight increase of weight brings us to potassium a solid metal and most energetically positive and it is quite unlikely that this should be due merely to a small additional condensation of such a body as hydrogen. It is contrary to the gradual change of properties observed in cases of polymerism or even homology in organic chemistry.

The supposition of two or more primal elements, condensed in varying proportions, is in accord with phenomena known to us but of course is so far without experimental or other basis if we exclude the mathematico-spectroscopic work of Grünwald. Take for instance, the widely different results obtained by varying the ratio between nitrogen and hydrogen in their compounds. Thus $3N$ and H give a well characterized acid and N and $3H$ give an equally definite base. This complete reversal of properties can no more be attributed to the hydrogen alone than to the nitrogen. The primal elements might act in this way in their condensation into the common elements.

There is no basis for the formation of any hypothesis as to the primal elements and speculations on this score are as idle as the dreams of the early Greek philosophers. The future may bring such knowledge as will afford the needed data. Certainly we are a long

step nearer to it in the recognition of the fact that the properties of the elements are dependent upon and determined by the atomic weights.

THE PERIODIC LAW.

A quarter of a century has passed since the first announcement of the Natural Law and the publication of Mendelejeff's table. The truth of the law in a general way seemed to be accepted very readily by chemists. It was incorporated in text-books and there explained, but comparatively little use has been made of it in teaching the science. Even Mendelejeff himself, in his *Principles of Chemistry*, has not made the fullest use of it. Victor Meyer, in his lecture before the German Chemical Society more than a year ago, showed how it might be used and how he used it himself, and probably, this will do much toward popularizing its use.

There must be some reason why so great a help to scientific study is not made more use of. Does it lie in a lingering distrust of the law itself or failure to accept it or is it because of the imperfections in the arrangements of the elements offered by Mendelejeff and others? It is most probably due to the latter and this paper is presented with the hope of clearing up some of these difficulties.

The modern chemical world has recognized in the discovery of Mendelejeff the greatest step forward since the announcement of the atomic theory. It is too much to expect that so great a discovery should spring full-panoplied from the head of its author. It has been accepted by chemists in all lands and is the basis of present chemical thought. Doubtless many have observed the im-

perfections of the law's original form or rather the table as first brought out. Probably some have ventured to comment upon it. Such criticisms have escaped me with one or two exceptions.

It is with much hesitation that I venture to point out what seem to me to be imperfections and blemishes in so great a work. Few may agree with me in calling them imperfections. I do not purpose to detract one particle from the greatness and importance of the essential truths contained in this discovery. Mendelejeff's table, as we have it at present, is a great advance upon the first one published by him in 1869 which must be pronounced tentative only and decidedly unsatisfactory. The table of Victor Meyer is far behind it in presenting the facts of the periodic law. There have been many attempts at devising a graphic representation of this law. I know of none which can be called real aids to the student or which do not introduce new ideas which, to say the least, have no basis in the facts as known to us at present. None of them can be regarded as a safe substitute for the simple table of Mendelejeff.

Taking that table I would venture to point out some obstacles to its present full acceptance. These have been in part revealed to me by the effort at an honest presentation of this great truth of nature to honest-minded, clear-sighted young men. Before mentioning these difficulties which lie here in the path of a teacher, I must preface that my criticisms are aimed at what I may be allowed to call the unessentials of the law. Mendelejeff's great feat was in seeing clearly and announcing intelligently that the properties of the elements were dependent upon and determined by the atomic weights. This is the essential of the periodic

law and is in accord with our fullest knowledge. The second part of the law as usually stated, that these properties are periodic functions, attempts in a measure to define the dependence. It may also be true but it is not fully proved and is open to objections. It seems to me that this hypothetical portion could well be left in abeyance until fuller knowledge gave it a stronger footing, meanwhile substituting something less open to criticism and which cannot weaken the central truth.

Take this table and examine it. First we find two kinds of periods made use of—periods containing seven elements and those containing seventeen. If it had only been possible to arrange all of the elements in sevens as Newlands attempted to do, the periodic idea would have been most convincing and the law of octaves running through nature would have seemed most wonderful. But these elements do not admit of being arranged in this way and the use of periods of different lengths is to fresh young minds, unacquainted with mathematical expedients, somewhat forced.

Secondly, there is a very anomalous position assigned to the triads or, as sometimes written, the tetrads, Fe, Co, Ni, (Cu,) etc. They have been set off to themselves, clearly so as to make the other elements fall even approximately into their places and into the proper sevens. I say approximately, for the student soon sees that although there is a similarity there is also a wide difference between the elements of the first and of the last seven in any period of seventeen.

Thirdly, in the lower periods, in order to get elements to fall into their places a great many unknown elements have to be interposed. Thus between cerium and ytterbium, the next element in the list, there are blank places for sixteen elements. The third large

period of seventeen has only four known elements in it and the fifth has only two. Of the five periods only one is completely filled out. To say the least, this shows a very imperfect knowledge of the elements, or a great deal of guess work. In the table there are sixty-four known elements and thirty-five blanks for elements yet to be discovered. I hardly think it possible that the majority of chemists believe that after all of our diligent search for the past century less, than two-thirds of the elements have been discovered. Where are the others in hiding? Will they be discovered by the spectroscope in the rare earths? There is certainly hope of finding some but the number to be found is appalling. The average student thinks, in all honesty, that the coincidences of the first part of the table will scarcely justify such forcing and wholesale interpolation. If our knowledge of the elements is as imperfect as that, we have no right to force them into periods. Some of them seem little inclined to fall into these periods of their own accord. How do we know that the remaining two-thirds may not upset the entire calculation? Certainly we are venturing a good deal upon a very imperfect knowledge of the remainder. Let us see how the matter stands. The periodic idea may be true but we do not know enough about these elements yet to be able to give this idea a very prominent place in the natural law, and we ought to avoid the assumption of so many unknown elements unless absolutely necessary.

As I do not intend to tear down without some effort at re-building, I would, with much real diffidence, for I realize that I may be looked upon as one who would rush in where only the great masters of the science can safely tread, offer the following table as a substitute:

My first suggestion is that the wording of the Natural Law be so changed as to read: "The properties of the elements are dependent upon and determined by the atomic weights." The somewhat difficult idea of function is simplified and periodicity is subordinated. Then I would substitute the following table for that ordinarily given. It is not greatly changed, and not much originality is claimed for it, but however slight the changes I would insist upon their value, because they do away with the dependence upon periods, and they certainly make the table an easier, more intelligible, and more useful one to the student. There is no forced effort at rounding off any period or group. There is room for additional elements when discovered, but the table is not dependent upon them.

Lastly, the inter-relation is more clearly brought out. I do not maintain that this table could ever have been discovered without the idea of periods, though I think it might. The periods still underlie it, but they are out of sight for the present and are not necessary. The table is not dependent upon them.

There are seven group elements having a mean increment of two in their atomic weights. It is by no means essential that there should be just seven of these. At present we do not know more, but I think there is possibly a place for one more having the atomic weight 21, differing widely from the others as it occupies a singular position.

These group elements are also to be called bridge elements as they show marked gradation of properties from one to the other and so serve to bridge over the groups and connect one with the other. Linked to them by an increment of sixteen are seven typical elements. These show the distinctive properties of the

groups to which they belong and a wider divergence from the next group to them. From them can be deduced the properties for the remaining elements of the group. Thus in group I Li is the bridge or group element and Na the type. From this type two lines of elements diverge, averaging three to the line. These triads would of course be changed into tetrads or pentads by the discovery of more elements. No importance is attached to the fact that at present they are in threes. There is a distinct increment for each line of elements. These can be averaged thus; Fig. 1 representing the arrangement and increments for the first three groups, and fig. 2 the arrangement in the last four groups, the increments varying slightly. These increments could be averaged in all except one case, and the agreements with known atomic weights would be close enough to admit of the easy arrangement of the elements in the prescribed order. Naming the triads Right Triad and Left Triad respectively we find that these averaged increments would be as follows: the increment from group to type element is sixteen; from the type to the first element in the Left Triad (L. T.) is 18; to second element L. T. is 63; to the third is 112;—to the first element to the Right Triad (R. T.) is 44; to the second R. T. is 88; to the third is 177.

Fig. 1.

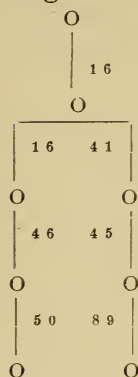
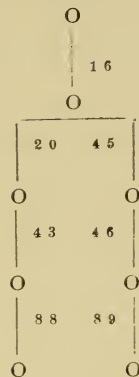


Fig. 2.



The one exception is in the increment from Type to III L. T. from group IV to VII. Instead of being 112 this is 141.

To the right of Group VII we have three triads which have nearly the regular increments belonging to the Right Triads, namely, 47 and 88. They are without any type element, it seems most likely that they belong to one group. The Group element would have an atomic weight of 21 and the Type one of 37.

The arrangement in the table then is partly one based upon regular increments in the atomic weights, and since these are so poorly known, partly upon our knowledge of the chemical properties of the elements. When it is recalled that about one half of the atomic weights are imperfectly known it will be evident that these averaged increments are approximations only. It is impossible to bring out such perfect symmetry as obtains in the homologous series in organic chemistry. And yet these groups should be something of the same kind. Following the analogy to the organic hydrocarbons a little further, may not the existence of an element in two different conditions as to valence, &c., as,

for instance, copper or mercury or iron be looked upon as a species of isomerism. Such speculations are of little use, however, and quite apart from our present purpose.

I have found this table very useful in teaching elementary chemistry and it can most profitably be made the basis of the entire course. Thus in the first four groups the left triad contains the elements most closely resembling the Types. In the last three they are to be found in the right triads. As to natural occurrence of the elements, in the first four groups those in the left triads occur in the same compounds and generally in connection with the type; those in the right triads occur as the type or as sulphides or are free. In the last three groups this is reversed. The right triad elements occur as the types and the left triad as the type or as oxides. So too the properties of the elements show this relation to the types. Take as an example the specific gravities in Group II.

Be 2.1	
Mg 1.75	
┌──────────┐	
Ca 1.5	Zn 6.9
└──────────┘	
Sr 2.5	Cd 8.6
Ba 3.6	Hg 13.6

It is not necessary to pursue this part of it at greater length. The careful teacher will easily work out

all these comparisons for himself and will find that chemistry taught by the table is shorter (so much repetition being saved) and is easier for the pupil and its symmetry and beauty is much more easily brought out. There is no special claim for originality made here. The germs of such a table or arrangement can be found in several text-books but I do not know of any in which the idea is fully developed or such a table as this is given.* I offer the whole as a suggestion. Perhaps some may find it useful who have met the same difficulties which I have encountered. Others may have overcome these difficulties in a still better way than this, and yet others may see no difficulty at all in the present table. I think, at least, all will agree with me that there are difficulties and very genuine ones also in the use of Mendelejeff's or Meyer's tables as given by the respective authors.

IMPROVEMENT IN THE METHOD OF PREPARING PURE ZIRCONIUM CHLORIDES.

CHAS. BASKERVILLE.

The preparation of pure zirconium chlorides from zircon is a rather long and tedious process. Linne-
man's method, [*Sitz. Ber. Kais. Akad. d. Wissen-
schaft.* Vol. II, 1885, translated in *Chemical News*
LII, 233 and 240. on "Treatment and Qualitative Com-
position of Zircon."] which is very long, was much
shortened and simplified by Venable [*Journ. Anal. and*

* The arrangements of Bayley, Hinrichs, and Wendt are some what similar but the ideas which I would make prominent, are obscured by other considerations and speculations.

Applied Chem. Vol. V p. 551]. Bailey's method [*Journ. London Chem. Trans. 1886, p. 149*] of precipitation by means of hydrogen peroxide is very expensive, aside from the difficulties one encounters in preparing the reagent pure.

Having learned that zirconium could be precipitated completely, freed from iron and aluminium, [*Baskerville J. Am. Chem. Soc. XVI, p. 475.*] by means of sulphurous acid, when working with the small amounts usually employed in analysis, I proposed to apply the same treatment to quantities in bulk for the purpose of obtaining a pure salt of zirconium.

The powdered zircon, washed with hydrochloric acid, (100 grams) was fused and treated according to the directions given by Venable [*loc. cit.*] up to the point where the impure zirconium chloride had been freed from silicic acid and was in a dilute hydrochloric acid solution.

This solution was nearly neutralized with ammonium hydroxide. A strong stream of washed sulphur dioxide gas was then led into the cold solution to thorough saturation. This required about fifteen minutes. Partial precipitation occurred in the cold, but other experiments had shown that the precipitation would be more complete if this solution saturated with sulphur dioxide was diluted largely and boiled. Five to ten times as much distilled water was accordingly added and the whole boiled half an hour in large evaporating dishes. The zirconium precipitated out and settled nicely. No bumping occurred during the cooking—while hot, the liquid was rapidly gotten away by means of an unglazed porcelain suction filter. The precipitate was washed two or three times with hot water, then boiled in water and again washed after

filtering. This precipitate was then dissolved in dilute hydrochloric acid and boiled to expel most of the sulphur dioxide. The solution was re-precipitated with ammonium hydroxide. The precipitated hydrates were washed free from ammonium salts and then dissolved in concentrated hot hydrochloric acid. Five crystallizations from the strong acid were found to be sufficient to remove the small amount of iron remaining.

Investigations are now in progress concerning the composition and nature of the precipitate produced by the sulphur dioxide.

A NEW POST OAK AND HYBRID OAKS.

BY W. W. ASHE.

During the past two years, 1893 and 1894, I have observed during several trips through the eastern sections of Virginia, North and South Carolina, a large number of oaks morphologically different from any described species, and in most of the cases, where mature fruiting specimens have been secured, the characters have required that they be referred to the already large list of oak hybrids. One of them, however, is a new form of the post oak, distinct enough to merit varietal place, and so described. The other forms, which I have examined, from which late fall leaves, winter buds and fruit were secured, have proved to be hitherto undescribed hybrids; while a large number are hybrids previously observed by others in different parts of the United States and to the elucidation of which my mea-

gre notes can add but little. I do not think the following hybrids have been previously reported from North Carolina: *Quercus Rudkinii*, *Q. sinuata*, *Q. aquatica* x *Q. Catesbæi*, *Q. minor* x *Q. alba*. The last one I find in the middle section of both North and South Carolina. In Mecklenburg county I found a fine specimen of *Q. coccinea* x *Q. phellos*, but its characters do not agree at all with the *Q. heterophylla* as described by Michaux in the Sylva or by Mr. Martindale. I have a large number of other forms from these and other states which I have not yet looked over or from which I have not yet succeeded in obtaining fruit or flowers.

To several of these hybrids, which are most constant in form, distinct in character and which are not intermediate in form between the parents, I have ventured to apply specific designation.

The following are the forms in my herbarium which I have looked over, with a few brief notes describing them:

Q. cinerea x *Q. Catesbæi*.—*Form 1*.—The sessile leaves, 3 to 5 inches in length, are narrowly oval to oblong, rarely oval in outline, with three short bristle-tipped lobes at the summit; or oval and entire. They are either rounded or acute at base. Above they are smooth and shining; below, whitened with the close white stellate pubescence of *cinerea*. The veins are straight and prominent while those of *cinerea* are obscure. The twigs and buds are coarse and large like those of *Catesbæi*; but the bark and general appearance of the trees is that of *cinerea*. The persistent leaves turn, in the fall, first a yellow and then by December a dull brown, at which date the foliage of *Catesbæi* is scarlet or partly green. The fruit, however, is that of *Catesbæi*, frequently, with a tumid base to

the cup, or the wall of the cup rolled inward around the margin. These trees are frequent. Ten or twelve were seen, which were essentially alike in foliage; and those which had fruit agreed in that.

Form 2.—The leaves are longer than in the above, 4 to 6 inches long; mostly oblong in outline; always three lobes at the summit, usually with long falcate lobes; either dentate or lobed on the margins. There are some scattering white pubescence of cinerea over the lower surface and tufts of coarse hairs in the axils of the veins. The bark is rough and black. The trees usually fork and have the general appearance of *Catesbæi*. The leaves turn scarlet in the fall like those of *Catesbæi*. The acorns vary a good deal but are more generally like those of cinerea. Several of these trees were seen.

Q. cinerea x *Q. laurifolia*.—Leaves oval or oblong, 1.5 to 2 inches long, acute at each end; deep green and shining above, below lighter and covered, especially on young shoots, with a scattering appressed tomentum. The leaves of young shoots are variously lobed, especially towards the summit. The midrib is very prominent, and also one or two pairs of lateral veins. No tufts of hairs are in the axils of the leaves. Twigs are covered when young with a thick white pubescence. The trees are small, 15 to 25 feet high, with broad, spreading, globose crowns, rather resembling *laurifolia*. Leaves remain bright green, or partly turn yellowish by December 6. Nut is brown, smooth, obscurely ribbed, subglobose; cup deep, covering from one-third to one-half of the nut; scales smooth, firmly appressed. Acorns are almost intermediate in character between those of the parents, except in pubescence. The fertile embryos are largely atrophied. Several

trees were found in different places, but always near the coast.

Q. cinerea x *Q. aquatica*.—The leaves 2.5 to 3 inches long, 1.5 to 2 inches broad, are broadly spatulate; rounded or three lobed at the summit; rarely rounded at base. Above they are smooth; below varying from the thick, white pubescence of *cinerea* to nearly smooth, with small tufts of coarse pubescence in the axils of the veins. The venation is mostly obscure. They are small trees, 20 to 25 feet in height, with drooping branches and rather smooth gray bark. The twigs are pubescent save where the pubescence has worn off. On December 2 the trees are nearly naked of leaves, the leaves still persistent being yellow, while type trees of *aquatica* are green. The nut is globose, brown, not ribbed, tomentose, as are the scales of the shallow or deep cup; cups persistent on the twigs as those of *aquatica* frequently are. Several specimens of this hybrid were seen, all near the coast.

Q. petiolaris.—*Q. cinerea* x *Q. tinctoria*?—The leaves are oblong or elliptical, 4 to 6 inches long and 1.5 to 2 inches broad; sinuate or crenate on the margins; mostly three lobed and dilated at the summit; truncate or subcordate at base. The lobes at the summit are usually bristle-tipped. Leaves are smooth above or with glandular, septate hairs along the midrib; the under surface covered with a close, brownish tomentum, wearing away with age; tufts of coarse pubescence in the axils of the primary veins. The venation is that of the black oaks (*tinctoria* and *coccinea*) with 4 to 6 pairs of prominent, impressed primary veins. The petiole is one-half inch long. The long buds, .3 inch, are lanceolate. The slender twigs are covered with the brownish tomentum of *cinerea*. Five or six

such forms were seen; all small trees with the bark and general aspect of cinerea. By December 1 the leaves have turned a light brown and are mostly persistent. The deep, nearly sessile cup, enclosing nearly one half of the nut, is top shaped and acute at base. The large, obtuse, pubescent scales are appressed or usually so. The cup is strongly spreading just below the margin. The nut is about one third larger than that of cinerea, oval, pubescent; the persistent base of the style is prominent. Only one tree was found in fruit and its nuts were mostly imperfect.

The character of the pubescence on leaves, twigs and fruit, the oval and entire form of a few of the leaves and the general appearance of the tree indicate cinerea as one parent. The other parent is one of the long-petioled leaved black oaks. Rubra, which probably does not occur, or rarely, where this was found, would be excluded by the deep cup. The shape of the leaf points to cuneata, but neither nut, cup or bud agrees in any particular. The forms of nut and cup are clearly toward those of tinctoria or coccinea, and especially does the thick wall of the cup and the angle made by the outer surface just below the margin indicate one of these species. I am inclined to say tinctoria.

Q. cinerea x *Q. nigra*.—The leaves are 3 to 4 inches long, 2 to 3 inches broad, usually broadest at the upper end. In shape they vary from elliptical to ovate, rarely slightly three lobed at the summit. The oval leaves are acute at base and usually acute at the summit. The others vary from rounded to cordate at base. Old leaves are smooth above except on the midrib which is covered with the close septate, stellate, brownish-gray pubescence of cinerea; below they are covered with a down of the same color. There is a dis-

inct petiole one-eighth of an inch long. The venation shows the dichotomous forking so characteristic of *nigra*. The upper bud scales are pubescent. The leaves are thick and stiff. In the fall they first turn yellow and then dull brown and persist. They are small trees, 6 to 10 feet in height, with drooping branches and rough bark. Only a few nuts could be found, only a few trees fruiting. These were oval and black ribbed, somewhat larger than the nuts of *cinerea*, and had disproportionately enlarged hemispherical cups, covered with coarse pubescent scales. The trees in November have the general appearance of *nigra* after the leaves have turned. Perhaps ten such trees were seen, all in the neighborhood of the coast.

Q. aquatica x *Q. nigra*.—The leaves are 2 to 4 inches long, 1.5 to 3 inches broad; broadly ovate or deltoid in outline, broadest above the middle. They are scalloped or slightly 3 (rarely 5) lobed and short bristle tipped; sessile and usually acute at the base. Above they are glabrous and also below, except in the axils of the principle veins where there are tufts of coarse hair. The leaves are thick and firm, and on November 24, were mostly green or the lemon yellow which withering leaves of *aquatica* turn. The venation is that of *nigra*. The buds are small but hairy at the summit as are those of *nigra*. The twigs are slender and warty. The pubescent—scaled cup is hemispherical, and encloses one-half of the ovate, obscurely ribbed nut. The nuts are imperfect, often with the fertile embryos but slightly more developed than the abortive ones. The branches are drooping; the bark is slightly gray. Only a single tree was seen, about 20 feet in height and with a broad spreading crown. Imperfect nuts and cups were abundant, the latter usually remaining on the tree.

Q. dubia.—*Q. phellos*? x *Q.*——. Leaves are entire, 3 to 7 inches long, and 1.5 to 3 inches broad. They vary in shape from lanceolate and linear lanceolate to broadly ovate or elliptical. The lanceolate leaves are shaped like those of *phellos*, broadest at the lower third; the larger ones are obtuse at each end and symmetrical. All are tipped with a single bristle. Above they are smooth; below there is some scattered pubescence over the entire surface and a line of coarse hairs along both sides of the midrib, as is the case usually in *phellos*. There are many pairs of prominent straight lateral veins. The venation is something like that of *tinctoria*. The stout petiole is nearly one-fourth of an inch long. The slender buds, .15 inch long, are pubescent, but the twigs are smooth. The distinctly peduncled cup is top-shaped or hemispherical, with involute margin; scales small, bright brown, closely appressed, almost smooth. The cup is .6 to .9 inch broad, .4 to .5 inch deep, and encloses one-half of the nearly globose, black and brown striped, hoary nut. It fruited abundantly.

Only a single tree of this remarkable form was seen. This was in the open, and was about 25 feet tall, with a spherical crown and spreading branches. The trunk, 10 feet long, had a rough, dark bark. The leaves were partially green and yellowish on November 20. They all turn a dark brown and drop. When green it resembles the evergreen magnolia. Although the shape of the leaves does not bear me out, I think this tree will prove to be a hybrid between *phellos* and *tinctoria* or *coccinea*. The texture of the leaves, however, is firmer than in any of those trees. There is no physiological debarment, that I know, which might prevent a third species from entering this combination.

That is, a hybrid *phellos* x *tinctoria* might in turn be fertilized by *cinerea* or *nigra*, and this tree be the result.

Q. falcata.—*Q. phellos* x *Q. cuneata*.—The leaves are 3 to 5 inches long, and 1 to 2 inches broad; oval or oblong to lanceolate in outline. The smaller leaves are entire, oval in outline, and acute at each end and have a very short petiole; while the largest are lanceolate with several shallow lobes towards the base and a long terminal, frequently falcate lobe, tipped with a single bristle. The petioles are from one-fourth to one-half an inch long. The nearly sessile cup is saucer-shaped, .5 to .6 inch in diameter and .2 inch deep with the closely appressed scales tubercled at base. The cup encloses only the base of the globose or sub globose nut which has the light brown color, in dead specimens, and wartiness peculiar to *cuneata*. Nuts are mostly imperfect and many, only half-formed. A large tree 60 to 65 feet in height with a large and spreading crown; bole 18 inches in diameter, with a rough dark bark resembling that of *phellos*. The foliage was a light green on November 20; dead leaves turn at once a dull brown.

Quercus minor var. *Margaretta*.—The leaves are 2.5 to 3 inches long, and 1.5 to 2 inches broad. They are oval in outline; entire, wavy-margined or with three spreading lobes at the summit. They are mostly acute at base, rarely obtuse or truncate. Above they are smooth, below they are soft downy. The slender petiole is from one-fourth to one-half inch long. The twigs are slender and smooth. The buds are acute and bright red, sharply 5 angled and large, .15 to .2 inch long. The cup is top shaped, rarely rounded at base, sessile or nearly so. The cup is .4 to .55 inch deep,

.45 to .5 inch broad and covers one-half or more of the slender brown nut which has a length of from .7 to .8 inch and a breadth of from .4 to .5 inch. The nut is silky canescent at the summit and is persistently beaked with the long and slender base of the style. This tree fruited abundantly in 1994, and was the only high ground white oak in eastern North Carolina that did do so. They are small trees 20 to 30 feet in height, growing in the high pine barrens of eastern North Carolina. When trees are killed by fire the roots usually sucker freely. The bark is similar to that of the type.

JOURNAL

OF THE

Elisha Mitchell Scientific Society

VOLUME XII—PART FIRST

JANUARY—JULY

1895

POST-OFFICE :
CHAPEL HILL, N. C.

ISSUED FROM THE UNIVERSITY PRESSES.
CHAPEL HILL, N. C.
1895.

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JOURNAL
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REACTIONS BETWEEN COPPER AND CON-
CENTRATED SULPHURIC ACID.¹

BY CHAS. BASKERVILLE.

Andrews² in writing on the "Assumption of a Special Nascent State," argued that the production of sulphur dioxide, as a result of the reaction between copper and concentrated sulphuric acid, was due, not to nascent hydrogen, as is commonly considered, but to the deoxidation of sulphur trioxide by the copper with the production of copper oxide as a primary product. Having noted frequently the evolution of sulphur dioxide gas before any evidence of this "copper oxide," at the suggestion of Dr. F. P. Venable, I began some experiments with a view of studying this complicated reaction, so simply treated in most text-books.

When my work was completed, in verifying my references I chanced on Pickering's¹ work on the same subject which had escaped me. Most of my work, especially that part which concerns the secondary reactions, is in accord with that of Professor Pickering. My observations concerning the primary reactions were not

¹ Read at the Springfield meeting of American Chemical Society.

² Chem. News, 70, 152; Iowa Acad. of Sciences, Proc. p. 4.

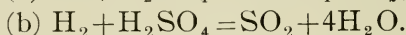
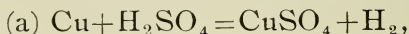
the same however. In making known the latter, I feel at liberty to give the results of my work, as independent corroboration is of some value.

The reactions which take place when copper is treated with concentrated sulphuric acid may be divided into primary and secondary.

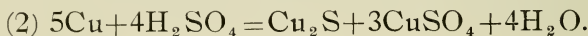
Primary:



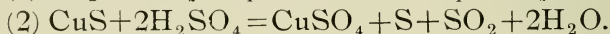
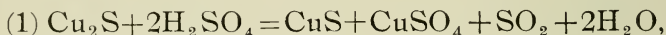
This may be regarded as taking place in two steps:



Still no hydrogen could be detected in the gas given off.



Secondary:



The experiments were carried out under various conditions of temperature and time, exposure of the metal to the action of the acid, and varying proportions of metal and acid. The copper ribbon used was cut into small pieces one cm. wide by two to three cm. long. Concentrated c. p. sulphuric acid, 1.84 sp. gr. was used. Each experiment, except where noted, was carried out in a flask in which the air had been displaced by a neutral gas, hydrogen or carbon dioxide. The evolved sulphur dioxide was led through a strong solution of sodium hydroxide and the sulphite formed titrated with a standard iodine solution or oxidized by bromine, and the sulphuric acid determined gravimetrically. A rapid stream of the inert gas was driven through the apparatus just at the close of the experi-

ment. Water was poured into the flask and the whole quickly filtered, and the copper remaining unattacked was then cleaned as well as possible by rubbing, dried and weighed. The copper, as sulphate, was determined by electrolysis. The residue was burned in a porcelain crucible, treated with concentrated nitric acid, ignited and weighed as copper oxide. Sulphur was determined by weighing a dried portion of the residue, treating with carbon disulphide, and the loss in weight taken as sulphur.

Primary Reactions. My experiments showed that the first of the primary reactions predominated when copper was treated with concentrated sulphuric acid at different temperatures (0° – 270° C.) At the highest temperature it was found that that reaction alone took place, but at all lower temperatures the second primary reaction also occurred. The proportion of the material following the second equation increased from 0° to 100° C., and then decreased to 270° C., when there was no longer evidence of any such reaction, that is, no black residue was formed.

At the lower temperatures, under 100° C., only the two primary reactions seemed to take place; at the higher temperatures the secondary reactions if the action were prolonged, frequently set in, complicating matters as far as quantitative determinations were concerned. If the time of action were shortened evidence of the occurrence of the primary reactions alone was found. Having an excess of copper present was also necessary, because as soon as all the copper had been attacked the secondary reactions set in at once.

The conditions seemed most favorable for the formation of the insoluble residue at the temperatures from 100° to 130° C. as may be seen from the table. The

proportion of the insoluble residue decreases rapidly in either direction from these temperatures. Some insoluble residue is produced at all the lower temperatures but none is produced when the reaction takes place at 270° C. and lasts for only a few seconds.

No.	Temperature of reaction.	Copper used.	Copper as sulphate. sulphide.		Sulphur dioxide produced.	Ratio of copper sulphate to copper sulphide.
1	0°-10°	0.1350	0.1340	0.0005	0.1343	268.0 : 1
2	"	0.0750	0.0740	0.0003	0.0780	246.0 : 1
3	20°-30°	1.3379	1.3260	0.0121	118.9 : 1
4	"	1.2473	1.2000	0.0184	1.2442	68.0 : 1
5	65°	0.1650	0.1600	0.0050	0.1648	33.0 : 1
6	70°-80°	0.0760	0.0730	0.0035	21.0 : 1
7	100°	0.1380	0.1060	0.0300	0.0840	3.5 : 2
8	"	0.3818	0.2800	0.1082	0.1166	3.5 : 1
9	"	0.9200	0.6400	0.2748	0.2165	3.3 : 1
10	120°-130°	5.2578	4.0800	1.1946	2.0932	3.5 : 1
11	140°-160°	5.0900	4.5100	0.5759	3.3084	8.0 : 1
12	160°-190°	1.1375	1.1200	0.0930	12.0 : 1
13	200°-220°	1.5450	1.4518	0.0932	1.0904	16.0 : 1
14	220°-230°	0.9815	0.9400	0.0332	0.9365	29.0 : 1
15	230°	3.8915	3.8200	0.0796	3.6327	49.0 : 1
16	230°	2.0000	1.9750	0.0388	2.2313	51.0 : 1
17	240°	1.1235	1.1035	0.0200	0.9855	55.0 : 1
18	250°-260°	2.1365	2.1000	0.0280	2.0304	80.0 : 1
19	270°	4.0000	None.

Berzelius¹ noted this black substance when copper was treated with concentrated sulphuric acid. He said it appeared to be a subsulphate because it was oxidizable by nitric acid. He made no quantitative determinations to show its composition. Such a body would contain fifty-seven per cent. of copper and in no case did I find the black residue to contain less than 67.64 per cent.

Barruel² found that sulphuric acid acted on copper at ordinary temperatures if sufficient time were given. He claimed that the sulphur dioxide produced was dissolved in the acid and attacked the copper forming cop-

¹ Traite de chimie 4, 324.

² Journ. de Pharm. 20, 13, 1834.

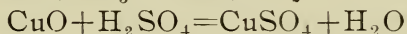
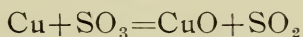
persulphide and oxide, the latter being dissolved in the acid.

Maumené¹ claimed that his black residue contained four different bodies; copper subsulphide and three oxysulphides, $\text{CuO} \cdot 2\text{Cu}_2\text{S}$ or $\text{Cu}_5\text{S}_2\text{O}$, $\text{CuO} \cdot 2\text{CuS}$ or $\text{Cu}_3\text{S}_2\text{O}$, and $\text{CuO} \cdot \text{CuS}$ or Cu_2SO .

In my analyses, as also in Pickering's, the sum of the percentages of copper and sulphur always approximated 100. In one experiment I did find a body whose composition approximated $\text{CuO} \cdot 2\text{Cu}_2\text{S}$. I shall speak of that apparent exception further on.

Calvert and Johnson² performed some experiments on the action of strong and dilute sulphuric acid on copper at temperatures from 130° to 150° C. They noted the formation of the subsulphide and claimed it was due to the liberation of free sulphur which afterwards combined with the copper direct.³ There was evidently something very wrong in their observations, for they failed to note any action below 130° C. Barriuel in 1834 had noted that action took place at the temperature of the air. I have noted the action at 0° C.

According to Andrews



are the correct formulas, SO_3 existing at the temperature necessary for the reaction, and the insoluble residue being the oxide. That would do if the reaction occurred only at those higher temperatures, whereas it occurs as well at 0° C. Besides this the undissolved residue is not the oxide at all, as he says it is, but

1 Ann. Chim. Phys., 1846, 3rd Series, 18. 311; Traite de chimie generale, Pelouze et Fremy, 2nd Ed., I, 388.

2 J. Chem. Soc., 19, 438, 1866.

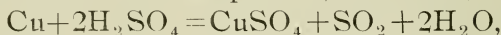
3 Pickering proved this impossible. The amount of sulphide produced was not increased by adding sulphur direct to the experiment,

invariably the sulphide. In making his analyses very likely he determined the copper alone and the percentage of copper in copper oxide and cuprous sulphide is the same. In a subsequent conversation with Dr. Andrews, I have learned that this was the case. This black residue when thoroughly washed free from any sulphuric acid always gave off hydrogen sulphide on treatment with hydrochloric acid.

The composition of the insoluble residue was determined by analysis:

	Found.	Calculated for Cu_2S .
Sulphur.....	20.44	20.14
Copper.....	79.56 (by difference)	79.86
	<hr/> 100.00	<hr/> 100.00

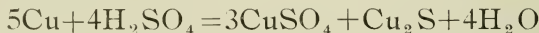
In the first of the two primary reactions,



it is seen that for each atom of copper found as sulphate, one molecule of sulphur dioxide should be evolved. Calculating on this basis from the following table we have the ratio of 2 : 3 between the copper as subsulphide and the copper as sulphate unaccounted for in the production of the sulphur dioxide.

No.	Sulphur dioxide.	Corresponding copper.	Total copper as sulphate.	Copper as sulphide.	Difference. Columns 3 and 4.	Ratio. Columns 5 and 6.
8	0.1166	0.1158	0.2800	0.1082	0.1642	2 : 3
9	0.2165	0.2132	0.6400	0.2758	0.4268	2 : 3

The formula



shows that relation between the two compounds of copper.¹

Second Reactions.—The secondary reactions depend

¹ Pickering states (loc. cit., p. 117) that once at 80° C. he observed that the copper in the two compounds stood in the relation of 2:2.9. I have not been able, however, to have concentrated sulphuric acid act on copper at any temperature from 0° C. to 270° C. without the evolution of sulphur dioxide, which is not accounted for at all in case the second of the primary reactions alone takes place, which he states did take place at 80° C.

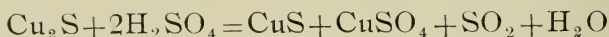
upon the second of the primary, that is, the cuprous sulphide produced. If the experiment were carried out so as to cause a rapid evolution of gas and the residue not allowed to form a protective coating over the copper, as long as an excess of the metal was present, only the primary reactions occurred. This was accomplished at 160°–170° C. If the strips of copper were touching they almost always became bound together by the anhydrous copper sulphate and a coating of the black residue formed a protective covering to the copper. When such a state of affairs occurred, no sharply defined line could be drawn to show, of these secondary reactions, when the first ends and the second begins, because as soon as some cuprous sulphide is changed to cupric sulphide, the latter is attacked by the sulphuric acid, sulphur being one of the products of the last reaction. Several experiments carried out at 140°–150°C. when this occurred with an excess of copper gave evidence of all the reactions, primary and secondary. Sulphur was deposited on the sides of the flask and the black residue contained 20.71 per cent. sulphur, and the theoretical percentage for cuprous sulphide is 20.138. This showed the presence of some cupric sulphide in which the percentage of sulphur is 33.59².

Some freshly prepared cuprous sulphide was treated with concentrated sulphuric acid. Sulphur was determined in the undissolved residue, the free sulphur being first removed.

	Found.	Calculated for CuS.
Sulphur.....	32.36	33.59

The formula,

2, Watts (vol. II, p. 41, 1875, Ed.) notes this complete decomposition.



explains such a change.

Another portion of cuprous sulphide was boiled with concentrated acid until it nearly all disappeared. The free sulphur produced was determined.

	Found.	Calculated.
Sulphur.....	19.71	20.138

The formula



shows the final result of the continued action of sulphuric acid on the subsulphide.

From these data the secondary reactions between copper and concentrated sulphuric acid may be expressed by the two formulas,

1. $\text{Cu}_2\text{S} + 2\text{H}_2\text{SO}_4 = \text{CuS} + \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$.
2. $\text{CuS} + 2\text{H}_2\text{SO}_4 = \text{S} + \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$.

The occurrence of sulphur on the sides of the flask at the end of the reaction may be said to be due to the sublimation of that element which is produced by the direct decomposition of sulphuric acid without the intermediate formation of hydrogen sulphide for the following reasons:

1. If hydrogen sulphide were produced by the decomposition of the sulphide, it is natural to expect some to escape in the gases which are given off. None could be detected.
2. As is well known, hydrogen sulphide is decomposed by concentrated sulphuric acid.
3. The deposit of sulphur is first noted on the sides of the flask and not in the delivery tube where the gases, hydrogen sulphide, and sulphur dioxide, would naturally come into the most intimate relations.
4. If flowers of sulphur be heated with concentrated

sulphuric acid in a flask provided with a long outlet tube, much of the sulphur will be seen to creep up the sides of the flask, and some sublimed even into the tube, which shows that the state of affairs observed may be attained without any trace of hydrogen sulphide being present.

COPPER OXYSULPHIDE.

Contradictory evidence to what has been stated above was found in one case where the insoluble residue approximated $\text{CuO} \cdot 2\text{Cu}_2\text{S}$ in composition. This is one of the oxysulphides stated by Maumené to exist in the black residue. The acid was heated to 250°C . in an Erlenmeyer flask. The air was not removed by an inert gas. The copper was suspended in long strips, only a third of which was immersed in the acid, the other part being exposed to the air.

The black residue formed under these conditions gave on analysis:

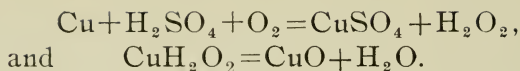
	Found.	Calculated for $\text{CuO} \cdot 2\text{Cu}_2\text{S}$.
Sulphur.....	16.16	16.15
Oxygen.....	3.54	4.03
Copper.....	undetermined	79.82

Schuster¹ found that copper was acted on by dilute sulphuric acid only in the presence of atmospheric oxygen. Traube² noted that copper was not oxidized in moist air, but was slowly in the presence of dilute sulphuric acid. Although copper is unable to decompose sulphuric acid at ordinary temperatures (according to Traube) its affinity for SO_4 and that of hydrogen for oxygen are together sufficient to cause such a decomposition, the probable reaction being:

1 Proc. Roy. Soc. 55, 84; Ber. d. chem. Ges., 28, 219.

2 Ber. d. chem. Ges., 18, 1887-1890.

3 Loc. cit., p. 138.



I could detect no oxygen in the gases given off when the experiments were carried out in an inert atmosphere. Nor could I detect hydrogen dioxide. Traube himself states that no "active" oxygen was liberated in the reaction because carbon monoxide was not oxidized to carbon dioxide. Pickering³ suggests that the sulphide formed is "oxidized at the time of its appearance by the oxygen which would be liberated at the surface of that portion of the copper which is immersed in the acid, since the whole arrangement would form a galvanic cell consisting of a metal, a liquid, and a gas."

UNIVERSITY OF NORTH CAROLINA.

SOME OF THE PROPERTIES OF CALCIUM CARBIDE.

BY F. P. VENABLE AND THOMAS CLARKE.

The calcium carbide used was prepared by the Wilson Aluminum Company. In this preparation, lime is mixed with some form of carbon, as coal-tar; the mass is then heated, with stirring, until a thorough mixture is obtained. The proportions are so arranged that the mass becomes dry and hard on cooling. This mass, in lumps, is then placed in the electric furnace. In a very short time after the turning on of the current, the process is complete. The molten mass can be run out of the crucible or it may be removed after cooling. On examination, it is easy to see that there is more or less carbon unchanged, or rather converted into the graph-

itic variety by the intense heat. Along with this are to be seen crystalline masses, lustrous and dark brownish black in color.

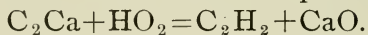
These are quite hard, and break with a crystalline fracture. Several efforts at effecting a separation from the graphitic carbon were unsuccessful. The lustre is slowly lost on exposure to air, more rapidly if the air be filled with moisture. The work will finally crumble down into a gray powder with particles of black graphite interspersed through it. The carbide can be kept for a year or two if placed in a tightly stoppered bottle and is quite easily preserved if a little coal-oil is placed in the vessel containing it.

By far the most interesting property of this carbide is its decomposition when brought in contact with water. The metallic carbides seem to be distinguished by the ease with which they exchange their carbon for the oxygen of water or for the radicals of various acids, the carbon combining with the hydrogen to form various hydrocarbons. Several authors have reported that the decomposition of this particular hydrocarbon caused the formation of acetylene. Experiments were carried out by us proving this fact, some time before there were any publications concerning it in the chemical journals, but we were not at liberty to publish anything concerning it at that time. If the gas, as evolved, is passed through a set of absorption flasks containing ammoniacal copper solution it will be entirely absorbed, not a bubble passing through, out of one or two liters of gas. Thus it seems to be pure acetylene. The amount of gas yielded by any one sample will be affected to some extent by the amount of graphitic carbon present. Hence different lots will vary some-

what. The average is about 200 cc. to the gram of carbide.

If the gas be ignited, as it is evolved, it gives a smoky flame; if it be considerably diluted, as one part of gas to from six to ten of air, a flame of great brilliancy and intensity is gotten. A company has been formed to introduce this as an illuminant upon the market. The cheapness of the materials used and the ease with which the gas can be found ought to make it a valuable and useful addition to our illuminants. If too large a proportion of air be admixed a very violent explosion can be brought about by igniting it. In some cases we have noticed the flame rapidly travelling backwards along a rubber tube towards the gasometer in which the gas was stored. One explosion taught us that care was necessary in handling the mixture.

Several analyses were attempted of the carbide, but for obvious reasons failed to give very satisfactory results. In the first place there was uncombined carbon present, also a small portion of a tarry matter, which could be detected by heating to high temperatures, and lastly, the specimens worked upon were several months old and in spite of careful keeping, had been slightly acted upon by the air and so contained uncombined lime or calcium carbonate. Moissan gives C_2Ca as the formula calculated from his analyses. This would agree well with the decomposition by water;



Action of Hydrogen upon the Carbide.—Dry hydrogen has no action upon this carbide in the cold. Several small pieces of the carbide were placed in a piece of combustion tubing, drawn out at one end to a point suitable for testing the flame. Dry hydrogen was then passed over it and as soon as the air was expelled the

hydrogen was ignited at the jet and a lamp placed under the tube so as to heat the carbide. In a little while the colorless flame became luminous and remained so a short time. A brownish, tarry matter condensed in the cooler parts of the tube. The mass of the carbide assumed a dull grey tint and a very thin white sublimate collected at a short distance from where the tube was heated. The ignition was carried on for five hours. The driving off of this tarry matter seemed to be the only action. The substance on removal from the tube, was still hard. On exposure to the air, it disintegrated, and, if thrown into the water, it was decomposed, showing the same behavior as the original carbide.

Action of Air and of Oxygen.—Some fresh pieces of the carbide were placed in the tube and heated while dry air was passed over them. A luminous flame was gotten as before and the same tarry matter was driven off and then there seemed to be no further action. Tests showed the carbide apparently unchanged at the end of prolonged heating.

Oxygen was then passed over some of the carbide which was being moderately ignited. No change was observed after two hour's heating. If the temperature was very high, such as that gotten in a combustion furnace, the carbide glowed brightly, as if burning, and a nearly white powder was obtained. The combustion was imperfect, however, unless the tube was very hot and the ignition prolonged. This refers not merely to the graphitic carbon mixed with the carbide but to the carbide itself. In several experiments the substance withdrawn from the tube, after heating some hours in oxygen, decomposed violently in water. It may be added, as was to be expected, that carbon dioxide had no appreciable action upon the carbide.

Action of Hydrochloric Acid.—Hydrochloric acid had no action upon this substance in the cold. When passed over the heated substance it caused it to swell up and assume a dirty gray appearance. A small amount of a liquid, apparently water, collected in the cooler portions of the tube and parts of the carbide fused down in glassy globules and masses. These were soluble in water and were easily shown to be calcium chloride. White fumes were evolved, some of which settled as a white solid upon the sides of the tube.

Action of Chlorine and Bromine.—When chlorine was passed over fresh carbide in the cold no action was observed. If even a moderate heat was applied, however, the lumps of carbide glowed very brightly, swelled, and fused together. A slight yellowish white sublimate was found in the tube. The fused mass was calcium carbide.

Bromine mixed with air was then passed over the fresh carbide. In the cold no action was observed. On heating, the carbide became red and the smaller pieces glowed. The lumps fused together and bubbles were observed on the surface as if some gas was escaping from the mass. Some condensed matter was found afterwards in the tube, and, on cooling, a peculiar odor was noticed different from that of the bromine. The fused mass dissolved readily in water and gave the tests for calcium bromide. Of course in this and the previous experiment the black specks of graphitic carbon were found unchanged. It was easy to distinguish them from the carbide. A few pieces of the carbide were dropped into strong, freshly prepared, chlorine water. There was a very violent disengagement of gas but it was not ignited as reported by Moissan. The gas was inflammable and burnt very much like acety-

lene. The odor was, however, peculiar. The same experiment was tried several times with a concentrated solution of bromine in water. The action again was very violent but there was no spontaneous ignition of the gas. Little difference could be detected between this and the action of the chlorine water.

Action of Acids.—A piece of the carbide was placed in concentrated pure sulphuric acid. A few small bubbles came off but the action seemed light. On heating, the action was greatly increased and continued after the removal of the flame. A gas was given off which burned with a luminous flame.

A mixture of sulphuric acid and potassium bichromate acted most violently upon the carbide. There seemed to be a very vigorous oxidation, and several attempts at igniting the gas given off resulted in failure. There could have been very little, if any, acetylene present in it.

Strong nitric acid attacked the carbide with the formation of brown-red fumes. The gas evolved could be ignited and burned with a smoky flame.

Glacial acetic acid decomposed the carbide slowly in the cold.

It may be added that no change was observed on adding a piece of the carbide to some boiling sulphur. On allowing the mass to cool the carbide was regained in its original condition.

Action of Alkalies.—A few grams of sodium hydroxide were melted in a nickel dish and a piece of the carbide was added. There was violent action, a gas being given off which burned with a luminous flame and which was taken to be acetylene.

A small amount of sodium dioxide was also melted in a nickel dish. When the carbide was added to this

it was rapidly attacked, the action being about the same as in the experiment just mentioned. An inflammable gas was evolved.

In conclusion, we would give due credit to Mr. W. R. Kenan, who carefully verified some of the experiments here recorded.

UNIVERSITY OF NORTH CAROLINA,
February, 1895.

ZIRCONIUM SULPHITE.

BY F. P. VENABLE AND CHARLES BASKERVILLE.

Very little is recorded in the text-books on chemistry with regard to this compound of zirconium. Berthier is reported as having examined it and found it to be a white insoluble body, slightly soluble, however, in an aqueous solution of sulphurous acid, from which it is thrown down again upon boiling. Whether this was what is commonly known as the neutral, or the acid, or a basic sulphite, is not recorded. It is highly probable that with so weak an acid as sulphurous acid, zirconium would form under these circumstances only basic compounds. We may state with regard to our own work that we have been unable with one exception to form any sulphite corresponding to the acid or the neutral. Only very indefinite compounds or mixtures of the sulphite with the hydroxide have come into our hands, as a rule.

The subject was first brought to our attention by the study of the reaction utilized by Baskerville for the quantitative separation of zirconium from iron and

aluminum.¹ It was also put into use by him for shortening the method of preparing the pure zirconium chlorides.² The reaction in question is that which takes place when a nearly neutral solution of zirconium chloride is boiled with sulphur dioxide in excess.

Several points of interest were observed as to this reaction. It was found that when a solution of the sulphate was used it was difficult to secure any precipitation by means of sulphur dioxide even with persistent boiling. The chloride was clearly the best salt to use. The pure chloride was made up into approximately a two and a half per cent. solution and this was either very nearly neutralized by means of ammonia, or ammonia was added until there was a slight permanent precipitate. In the latter case the saturation of this solution with sulphur dioxide produced an immediate precipitate. If this were permitted to stand for some time the precipitate was redissolved, the remaining liquid being only slightly clouded. This re-solution was probably due to the hydrochloric acid liberated and also to the excess of sulphurous acid present. If this solution of zirconium chloride saturated with sulphur dioxide were diluted with several times its volume of water and boiled from fifteen to thirty minutes, a heavy white precipitate was produced. This was quite easily filtered by means of an unglazed porcelain suction filter. The precipitate was washed several times and finally dried over sulphuric acid in a desiccator. The analysis gave:

Zirconium dioxide...	61:10	61:75	61:75	61.00
Sulphur dioxide.....	22.24	22.20
Ratio of zirconium to sulphur dioxide is 2 : 1, approximately.							
Ratio of zirconium to sulphur dioxide in the neutral sulphite, Zr (SO ₂) ₂ , is 1 : 1.4.							

1. J. Am. C. Soc, 16. 475.

2. THIS JOURNAL, 11, 85.

This substance when so dried was perfectly white and quite hard. It was powdered with some difficulty in an agate mortar and resembled, very much, finely divided silica.

It was sometimes noted that the precipitate formed on passing the sulphur dioxide into the solution of zirconium chloride was partially dissolved upon the prolonged passage of the gas. To determine in how far the liberated hydrochloric acid was the agent causing this re-solution, some zirconium hydroxide, freshly precipitated by means of ammonium hydroxide, was washed free from hydrochloric acid and was then treated with a concentrated and freshly prepared solution of sulphur dioxide. This was allowed to stand during two or three months and was frequently shaken. The solid at the bottom of the flask separated into two layers, the gelatinous hydroxide settling first and upon this a white, finely divided, substance formed. The supernatant liquid was found to contain zirconium. The white layer was separated from the hydroxide and analyzed. It contained:

Zirconium dioxide	15.05	15.53
Sulphur dioxide	4.86
Water (blast-lamp).....	2.78	3.03
Water, at 95° C.....	77.41	76.33
	<u>100.10</u>	<u>99.75</u>	

Ratio of zirconium to sulphur dioxide is 2.2 : 1.

This substance apparently came to a constant weight on drying in a steam-bath at 95° C.

A somewhat peculiar product was obtained during an attempt at filtering the precipitated sulphite. It filtered very slowly and in the course of a few hours a layer of a watery liquid formed above the white sulphite. This was allowed to stand several days and turned into a solid jelly. This was noticed several

times. The thickness of the jelly-like layer, would of course, depend upon the amount of moisture in the precipitate but several times it was half an inch or more in thickness. This body was analyzed in the moist condition after simply drying between filter paper. It gave:

Zirconium dioxide.....	20.02	20.65
Sulphur dioxide.....	5.19	5.51
Water (blast lamp).....	9.14	8.53
Water, at 95° C.....	65.65	65.22
	<u>100.00</u>	<u>99.91</u>		

Ratio of zirconium and sulphur dioxide is here 3 : 1.

A portion of this jelly was brought to constant weight by heating for a number of hours in a steam-bath. About sixty-five per cent. of the original weight was lost and the body assumed a translucent appearance like dried gelatine. The analysis of this gave:

Zirconium dioxide.....	59.34
Sulphur dioxide.....	11.46
Water (blast-lamp).....	29.20
	<u>100.00</u>	

Ratio of zirconium to sulphur dioxide is 4 : 1.

The analysis shows that some of the sulphur dioxide was lost on drying.

It will be seen that these different preparations show a very varying ratio of the zirconium to the sulphur dioxide and in no case approach to the ratio of the neutral sulphite (1 : 1.4). They are, therefore, to be looked upon as either mixtures of the sulphite and hydroxide or very unstable compounds. The jelly-like substance mentioned last gives more promise of being a chemical individual; still it has not been thought legitimate to attempt the calculation or assignment of a formula to it.

A last attempt at preparing the neutral sulphite was made by placing some of the excess of sulphurous acid,

which had been standing over the precipitated zirconium sulphite, in a dessiccator and allowing it to evaporate over sulphuric acid. The bulk of liquid decreased from about 200 cc. to five to ten cc. and then hard, white, warty crystals began to form, which were quite difficult to remove from the crystallizing dish. In appearance they resembled zirconium sulphate. The solution had lost the odor of sulphur dioxide. The time consumed in the evaporation was several months.

The crystals were dried upon filter-paper and yielded, on analysis:

Zirconium 24.47 per cent. on a dry basis, 36.43.

Sulphur dioxide 34.54 " " " " " 51.42.

Calculated for $Zr(SO_3)_2$, Zr 36.25; SO_2 51.20. These crystals then seemed to be a hydrated sulphite of the composition $Zr(SO_3)_2 \cdot 7H_2O$.

The nature of the precipitate gotten by means of sodium sulphite was also examined. The sulphite used was fairly pure. The zirconium chloride solution was distinctly acid and the mixed solution was acid. A transient precipitate was produced in the cold on mixing the two. On heating, a good flocculent precipitate was formed which settled well and was easily filtered. The precipitate looked like the hydroxide, rather than the white sulphite already described. The analysis gave:

Zirconium dioxide.....	5.75	5.75
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Sulphur dioxide.....	1.05	1.004
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Ratio of zirconium and sulphur dioxide is 4 : 1.

Chancel,¹ in giving a method of separation of iron from zirconium, states that by means of a boiling solution of sodium thiosulphite the zirconium is precipitated as thiosulphite. Stromeyer¹ stated that if a dilute

¹ Ann. d. Chem. u. Pharm., 103, 237; Watt's Dictionary, 5, 1081, 1877.

¹ Ibid. 113, 127.

zirconium chloride solution be neutralized by sodium carbonate in the cold and sodium thiosulphite added until the solution was decolorized and then boiled as long as sulphur dioxide came off, the zirconium would be precipitated as oxide (meaning doubtless hydroxide).

To test these observations a solution of zirconium chloride was neutralized by ammonia and an excess of sodium thiosulphite was added in crystals. A precipitate began to be formed directly. This was washed eight or ten times by decantation, filtered, the precipitate dried by absorption paper, and analyzed. It gave:

Zirconium dioxide.....	19.66	20.50
Sulphur dioxide.....	4.03	4.14
Water (blast-lamp).....	16.05	16.41
Water, at 95° C.....	60.11	58.58
	<u>99.85</u>	<u>99.61</u>		

Percentage of zirconium on a water-free basis is 75.

Percentage of zirconium calculated in $Zr(S_2O_3)_2$ is 21.95.

A second experiment was carried out with an acid solution of zirconium chloride. The sodium thiosulphite crystals were added in the cold and when completely dissolved the solution was heated to boiling. This precipitate, on analysis, gave:

Zirconium dioxide.....	21.74	20.73
Sulphur dioxide.....	5.33	5.41
Water (blast-lamp).....	9.72	8.64
Water, at 95° C.....	63.28	65.37
	<u>100.07</u>	<u>100.15</u>		

Finally another portion was taken, precipitated with an excess of sodium thiosulphite, and boiled until there was no longer any odor of sulphur dioxide. This precipitate was analyzed:

Zirconium dioxide.....	47.01	47.19
Sulphur dioxide.....	6.90	6.95
Water (blast-lamp).....	21.41	21.14
Water, at 95° C.....	24.16	24.72
	<u>99.48</u>	<u>100.01</u>		

The percentage of water here was due to the exposure of the precipitate in a warm room and its consequent partial drying. There is no evidence here nor in the previous cases of the formation of any definite thio-sulphite and we would question its existence under ordinary conditions. There is no evidence of the formation here of an hydroxide as one of the authors quoted states. Basic salts seem to be the only products.

UNIVERSITY OF NORTH CAROLINA,
March, 1895.

THE CHLORIDES OF ZIRCONIUM.

BY F. P. VENABLE.

In a report upon the examination of the chlorides of zirconium¹ it was stated that pure zirconium tetrachloride was formed by the solution of zirconium hydroxide in hydrochloric acid and repeated crystallization from the concentrated acid. This statement was based on a partial analysis by Linnemann², the result of which made him call the substance the tetrachloride; and on repeated partial analyses of my own, in which the zirconium present was determined by ignition as zirconium dioxide. So firmly convinced was I of the fact that this was the normal tetrachloride that I determined to use it in revising the atomic weight. Ten closely agreedeterminations were made and they yielded as the percentage of zirconium dioxide found 52.99, or, calculating with 90.62 as atomic weight of zirconium (Bailey)

1. J. Am. Chem. Soc. 1894. 16. 460-475.

2. Lond. Chem. News. 52. 233-240.

39.16 per cent. of zirconium. The zirconium in the tetrachloride amounts to 38.99 per cent.

Bailey made several very widely differing determinations of the chlorine in this body and considered it the oxychloride. His determinations varied so greatly and his mode of drying were so faulty that I simply concluded he was mistaken, being unable to detect a source of error in my analyses which would allow for a change from 39.16 per cent. of zirconium to 46.79 per cent., the amount needed for the oxychloride.

Still, as a necessary precaution, I made some determinations of the chlorine in the pure crystalline product and was greatly surprised to find only 35.5 per cent. of chlorine instead of 61.01, the amount required for the tetrachloride. The percentage in the oxychloride would be 36.63.

I regard the results as very singular. The substance must be an oxychloride, but what is its composition? The simplicity of its preparation and the constancy of its composition, along with its stability, would argue for a simple formula. No such formula can be calculated from the analysis. Probably the best formula suggested for this oxychloride, corresponding closely with the above analysis, is $Zr_3(OH)_5Cl \cdot 5H_2O$.

UNIVERSITY OF NORTH CAROLINA.
August, 1895.

THE DRUDGERY OF SCIENCE.

The study of Natural Science presents so much that is attractive and entertaining that a distaste is some times begotten in the mind of the beginner for the sober, plodding side of it. A lecturer upon Geology

or Chemistry is at the disadvantage of having an audience which expects to be amused, as at some exhibition of jugglery, whereas the language teacher has under him those who realize fully that there is no royal road to learning. I have heard a distinguished professor of chemistry say that he always felt his class begin to drag when he passed the "fizz, pop and bang stage." They would gaze in wonder at the beautiful experiments upon the elemental gases but had no stomach for the hard work of the science. And yet, how essential this plodding, this toil without apparent, or at least immediate, reward, is to the truth of the picture and to the success of the study. The drudgery ceases to be such in the eyes of the enthusiastic searcher into nature's mysteries. It becomes a joy, as bringing him a step nearer to the realization of his hopes.

If any of you are looking forward to a life-time of work in the realms of science it is well that you should face clearly the condition demanded of you for the highest, truest success, namely, patient and often times seemingly fruitless toil. A patient worker who has just laid his tribute on the altar of science, before an admiring world of fellow-citizens—I refer to Morley and his monumental work upon the atomic weight of oxygen—writes:

"Do not deceive yourselves, however, by thinking that patient toil can accomplish everything. Genius is not 'an infinite capacity for taking pains' but a something broader and deeper, that lifts the drudgery into the sublime. You may take infinite pains and still be only a drudge. You must take infinite pains to be a brilliant leader."

One of the most valuable qualities of mind to a man of science is persistence, obstinacy, doggedness—what-

ever you may choose to call it. It means an unyielding determination to persevere in spite of difficulties and discouragements. Accuracy of observation, clearness of intellect are all good and necessary, but unless you have genuine grit, and stick at the task you have set yourself, you can make no very valuable conquest from nature nor contribution to the store of human knowledge. It is the patient settler who has cleared the land, tilled the soil, sown the seed, toiled, suffered and waited and thus has won for the world its great feeding-ground in our Western States, and so it is the patient Darwin, the toiling Agassiz, the untiring Liebig, who have opened to us such great vistas in the domain of science. If we would follow them we must toil over the stepping stones they have succeeded in laying. If we would go yet further and discover Nature's secrets for ourselves, a capacity for patient drudgery must be ours. And yet, though it seem drudgery to others who are merely looking on, it is not really such, for to us it must be a labor of love.

I wish to bring before you some eminent examples of drudges that you may draw encouragement from them. Many instances might be drawn, first, from the life of Darwin. Take, for example, his patience when he reports himself as watching for two hours to see whether a spider put the right foot or the left foot in front in weaving, and his honesty in confessing, at the end of it, that he could not tell. Consider those fifty years during which he watched the lowly earth worm and found out for us its beneficent action in preparing our soils.

Patient drudges, or shall we call them heroes, are to be found in all the branches of science. Think of Lubbock and his work with ants and bees; of Ehrenberg

and his blinding himself with his microscopic investigation of infusorial earths; of Galileo and his telescope. My acquaintance lies mostly, however, with chemists, and I shall draw from among them the examples we need.

Some years ago Dr. Kerr, our former State Geologist, supplied a distinguished English chemist, Dr. Crookes, with a large amount of a rare mineral, samarskite, found in this State. Years were spent by this gentleman in, what he speaks of as the most trying and laborious of work, fractional precipitations, in order to separate the rare elements contained in the mineral. This meant a repetition for many hundreds of times of the same delicate and trying operations. The final report of the work occupied only a few pages and gave to the uninitiated little sign of the labor spent upon it.

Another instance of the same sort of work came to my notice a few years ago. Dr. Shapleigh, an ambitious American chemist, wrote me that he too had been working on the rare earths (from cerite and monazite also gotten from this State) trying to separate praseo- and neo-dymium and to prepare their compounds, with the hope of thoroughly studying them. After three years of daily toil and over 400 precipitations from 8 or 10 tons of materials, he had them separated and the compounds prepared and then found himself unable to continue the work and earn the reputation which he so richly merited.

A German chemist wishing to find out some of the constituents of the sugar-beet worked over six thousand pounds of them in small portions, by prolonged and patient operations.

We have some remarkable instances of patient toil among the older chemists also. Thus Boerhaave dis-

tilled the same lot of mercury five-hundred times to contradict the old alchemical notion that an essence could be gotten from it, and other mercury he kept at a raised temperature for fifteen years, watching for any changes, meaning countless repetitions of the same tiresome work.

I knew, myself, a young German student who, for weeks and weeks, was practically an outcast, working in a part of the laboratory to himself, unable to eat with his fellows, a burden to himself and to others because of the loathsome chemical substances he had chosen to work upon. We always threatened to put him under the sink or soak him in the water butt if he came near our part of the laboratory, and so I know little of his work or success, but he showed the scientific spirit and pluck. The work had to be done to gain the desired knowledge. It was loathsome, it was drudgery, but someone had to do it, and why not he?

I have heard of an American student who spent months in distilling and examining foetid bone oil. It seems to me, as a would-be scientific man, I should be forced to draw the line at bone-oil.

Only a year or two ago, I reported to the Society the patient toil of an English worker who was trying to understand the processes in the germination of grain. His microscopic dissections counted up into the hundreds, and yet, though spoken of casually and as a matter of course, seemed to me a marvellous proof of skill and patience.

But this drudgery may meet you at the outset of your career, and not only after you have become veterans, and if we listen to the older masters of Science, it is best for us that we should be so tried.

My teacher was one of the pupils of the great Ger-

man chemist Wöhler. He told me that when he first entered Wöhler's laboratory, the dried-up looking but brilliant German set him to grinding some hard substance in a mortar, and kept him at that and nothing else for three solid weeks. Perhaps it was the memory of this that made him set me, first, at a task of distilling water and keep me watching its drip, drip, for one long and weary week.

How such training can be of use, is told us in the charming and all too short autobiography of Justus v. Liebig, published by the German Chemical Society. His father was a dealer in colors. The boy, driven by the workings of the chemist spirit within him, experimented with his father's slender store of chemicals, and as the possible mixings and changes were necessarily limited, never wearied of repeating them, learning thus exactly the appearance and the changes they underwent, and acquiring perfected powers of observation to which he largely owed his after successes. He says, that it taught him especially to detect without fail similarities between bodies. Wöhler's training led him to take the contrary view and always to see the differences between the different kinds of matter before him. As much of their work was done in common, these two great men supplemented one another in their trained faculties, and from the farmer to the manufacturer, from the poor man who enjoys cheap clothing and better food to the suffering patient who is restored to health, mankind arises and calls them blessed.

Please note that this toil and drudgery is something different from the hap-hazard work of the alchemists and gold-seekers of the middle ages, and yet all of you have heard the tales that go to show how all-consuming was the pursuit of that flighty, illogical work.

That which I have been referring to is logical, carefully planned work, with definite ends in view.

I will close by recounting for you, in part, the story of Palissy, the potter. It may be a twice-told tale to you, but it well illustrates scientific drudgery pursued either to death or to success. Europe was without porcelain. The only pottery known to French art was common earthenware. Palissy set for himself the task of discovering how the beautiful enamel was made which could be seen on priceless ancient pieces or on imported Eastern ware.

How was he to begin? He had no teacher, he had no property. He himself says:

“Without having heard of what materials the said vessels were composed, I pounded, in those days, all the substances which I could suppose likely to make anything, and having pounded and ground them I bought a quantity of earthen pots and broke them to pieces. I put on them some of the materials that I had ground and having marked them, I set apart in writing what things I had put upon each, and having made a furnace to my fancy, I set the fragments down to bake.”

He built his furnaces, exhausted his resources and *failed*. He pulled down his furnaces, broke fresh pots, undeterred by an empty purse, an empty cupboard and a remonstrating wife, and *failed again*. Then he prepared three or four hundred pieces and sent them to a neighboring potters-kiln to be burned, after, as he says, he “had fooled away several years, with sorrows and sighs because he could not arrive at his intention.” The result was that he “received nothing but shame and loss because they turned out good for nothing.” This he did several times with failure only for his reward. Then hunger at home and the clamors of Mad-

ame Palissy could no longer be disregarded and he gave up for awhile.

For a year and a half he was conjugally a happy man, but scientifically wretched, for the fire of genius within could not be quieted. Having earned some little money by other work, he turned again to his enamel. For two years he continued his experiments and Madam Palissy scolded. His house was stripped, his children hungry. He agreed to make one final experiment, and if it failed to give up that for which he had labored five long, hard years. His trial was a partial success and nerved him to further efforts.

Time fails me to follow him through all of his trials and disappointments. I do not know of any more pitiful and yet more wonderful and stirring account of man's triumph over obstacles that most would call insurmountable.

He blundered thus for fifteen or eighteen years. He wasted away until there was no form nor prominence of muscle on arms or legs. He received no help nor consolation at home nor abroad, and yet he triumphed at last. The secret was learned, the art was won. Noblemen visited his cottage. Madame Palissy smiled again and purchased a "fine grass-green camlet" as some sort of amends for her furniture, burned in his furnace, and her years of home happiness sacrificed. He removed to court, was highly favored by the king, and France and Europe were filled with his fame.

May you have something of his energy and his perseverance and be blessed with wives more patient and more helpful than Madame Palissy.

NOTES ON THE UNDERGROUND SUPPLIES OF POTABLE WATERS IN THE SOUTH ATLANTIC PIEDMONT PLATEAU.*

BY J. A. HOLMES.

It is a fact that is coming to be more widely recognized by the general public as well as by members of the medical fraternity, that the health of persons living in our hill country depends in no small degree upon the drinking water obtained,—just as it has been found that the use of pure water in the lowlands and swamp areas of the Southern states results in practical immunity from malarial diseases. Hence the problem of how to obtain supplies of wholesome water for the towns and manufacturing establishments in the hill country or Piedmont plateau region of the south-eastern states comes to be one of considerable interest, the importance of which will continue to increase as the favorable conditions for manufactures and agriculture in this region will make it in the near future the most thickly populated portion of the South Atlantic states.

Water supplies from surface streams are unquestionably of the first importance; and in the mountain counties where the region is still largely forest covered and the streams rapid and continually aerated by rapids and cascades, the water is of superior purity and clearness. This statement is also applicable to the more elevated and sparsely settled portions of the Piedmont plateau; but in the less hilly and more thickly settled portions of this region the streams are more sluggish and the waters more muddy and less pure owing to the fact that a much larger proportion of the surface is

* From Trans. Am. Inst. Mining Engineers, XXV., 1895.

under cultivation. Furthermore, many of the towns and manufacturing establishments are located at distances from the larger rivers and creeks too great to permit of the water being lifted and transported to them by pipe lines at any reasonable cost.

Rain water caught from the roofs of houses, under favorable conditions, and kept in properly constructed cisterns, is probably the safest for drinking purposes, but under unfavorable conditions and when not properly attended to, cistern water must be considered as not altogether safe; and in any case the supply is inadequate for large establishments.

Such being the case with regard to surface supplies of water, it will be seen that, in a number of cases, we must depend for potable waters upon underground supplies. These may be obtained either from springs or wells. Of the latter we may consider three varieties: The ordinary open well such as is often seen about private residences; deep bored wells which penetrate the crystalline rocks, in the endeavor to obtain artesian supplies of water; and the shallow bored wells which are put down through the soil to the surface of these crystalline rocks in the hope of striking underground currents along the lines of contact between the lower portion of the soil and the upper portion of the undecomposed rock. In this latter case generally several such wells are bored within a short distance of each other and these are connected by iron pipes, and water is pumped from the various pipes through a common pipe to a common reservoir or tank. This is what is generally known as the tube well system.

The open springs furnish an excellent but limited supply of water for family use; a supply, however, which while it is sufficient for the needs of isolated residences,

it is generally inadequate to meet the demand about towns and manufacturing centers, and futhermore, in such latter cases, and frequently even near isolated country residences, the surface in the neighborhood of the spring becomes so contaminated with decaying organic matter that the water becomes unfit for drinking purposes. The same general statement may be made concerning ordinary open or driven wells, which for the sake of convenience must be located near residences where the surface soil becomes more liable to contamination as the region becomes more thickly settled. Examples of this are not infrequently seen, where the water from wells and springs in newly settled communities is found to be healthful, but a few years later it has become so contaminated with organic matter, which has permeated the soil from above, that sickness follows its use, and it must be finally abandoned. It is difficult, however, to get the average citizen to understand that the organic matter of the water in his well or spring comes from the soil immediately about his premises, as the prevailing notion concerning these supplies of water is that they come, not from the immediate vicinity, but from some distant region. Consequently in many of our towns and even about the isolated country residences, the barn yards and the privies and the hog pens seem to be built upon the principle of convenience alone, and this frequently places them in close proximity to the well or spring from which the family supplies of drinking water are obtained.

But outside of this the question as to the purity of the water, the supply of water from the isolated springs and open wells is generally quite inadequate for towns or manufacturing establishments of any considerable

size unless the number of these wells is greatly multiplied, and their multiplication means their wider distribution through the settlement or community, and thus a multiplication of the possible sources of disease from the drinking of contaminated waters. Nevertheless, the fact remains that, many of the towns of this region, with a population of from a few hundred to several thousand, are still without any general supply of water other than that from independent shallow wells. And while the amount of disease in such cases generally increases with the age of the town, and the physicians, at least, recognize the increasing contamination of the water as the source of this increase in sickness, yet for the lack of a better system this one continues in existence.

Deep artesian well supplies are not to be depended upon for the reason that the geologic conditions in the the Piedmont plateau region are not favorable. The rocks of this region are crystalline schists, gneiss and granites with the dips (schistosity) generally steep and varying on both sides of the vertical. A considerable number of borings varying from 100 to 1000 feet, have been made into these crystalline rocks in the Piedmont region of the two Carolinas and Georgia during the past few years, with the expectation of securing either an "artesian" (overflow) supply, or a supply that would come near enough to the surface to be reached by pumps. But the results have been generally unsatisfactory, the holes being "dry" or the supply of water being inadequate. A somewhat exceptionally favorable result was experienced in Atlanta. Some years ago (1881-82) a well was bored into the gneiss rock in the heart of Atlanta to a depth of about 2200 feet, at a cost of about \$20,000.00. At a depth of 1,100

feet a large supply of water was tapped, and it rose to within about 17 feet of the surface. For several years this well constituted the water supply for a considerable part of the city, but the water was pronounced unsafe by the medical authorities, and the well has been abandoned for a water supply from the Chattahoochee river. In a few other cases exceptionally large supplies of water have been reached; but as a rule the boring of these wells has failed of satisfactory results.

Some professional well borers, like some professional miners, with a laudable desire to be kept busy, urge that the deeper the hole the better are the chances of success; an opinion that has frequently but slight foundation in the case of the mines, and in the case of well boring it is, in this region of crystalline rocks, contrary to both theory and experience. The possibility of exceptions no one will deny, as we see that in a few of the deeper mines of this region considerable streams of water are tapped; and in some cases there is a bare possibility that the hole to be drilled for a water supply may tap such an underground stream of water, as was the case in Atlanta; but the chances are more than 10 to 1 against such "luck." As a rule these crystalline rocks become harder and more solid as we descend, the chances of securing a reasonable supply of water—never good after the hole enters the real mass of rock—may be said to decrease as the hole descends. There is, however, one certainty about this operation, and that is, other things being equal, the deeper the hole the more rapidly the cost increases.

During the past few years the tube well system mentioned above has been introduced in a number of communities in this piedmont region and with decided success in furnishing a good supply of drinking water

to the smaller towns and manufacturing communities. This system is based upon the existence of fairly well defined underground "currents" of water in regions where the topography is favorable and where the rocks have decayed to a considerable depth, and where near the lower limit of this decay there is more or less porous material through which this water may readily percolate. Of course it has been well known in the past that more or less well defined underground movements of water existed, and that at favorable locations the small currents come to the surface as springs, and that frequently, on both elevated regions and about lowlands, when wells are sunk sufficiently deep into the soil,—usually near the surface of the hard rocks,—a sufficient amount of water is found either to empty into the well as a small stream or to ooze into it from the surrounding soil and thus furnish a limited supply. But it is only recently that the location and extent of these underground sources of water have been investigated in some regions with considerable care and have been found to yield under proper treatment much larger quantities of water than have been reckoned upon in the past. This investigation has been prosecuted in this region mainly by Mr. Henry E. Knox, Jr., a hydraulic engineer, of Charlotte, N. C., and he has in this way located considerable supplies of underground water in regions where these were sorely needed.

I give below, in tabulated form, the results obtained by Mr. Knox in Piedmont North and South Carolina. His method of investigation is to examine carefully the topography and geology of the region where the water supply is needed. The topographic conditions favorable to success are, as might be expected, where there is more or less of the basin, shallow ravine, or valley,

so that the water that falls upon this surface, instead of running off in opposite directions, if the soil is sufficiently porous naturally percolates downward and tends to concentrate along the lower portion of such basin or valley where it may meet with least resistance in the more porous materials.

By way of exploring such a region, a number of holes are bored in line across the basin or valley, so as to determine the existence and location of such an underground "current" of water. In this way its position at intervals is determined and the intervening course is traced by additional borings. If the water supply is tapped by these borings it sometimes overflows; the output of the pipe at the surface of the ground and the quantity thus overflowing is measured, and pumps are then applied so that the possible yield of water can be estimated. In these underground 'streams' the water usually follows the topographic conditions, as might be expected, but in some cases it moves more or less obliquely across the ravines, showing that the overlying soil has not the same thickness everywhere, and that the topography of the soil surface is not the same as the topography of the underlying rock surface; and the water current moves along down the incline of least resistance of the rock surface, in a measure independently of the topography of the surface soil.

The fact that that the water percolates through this more or less porous material at considerable depths below the surface, of course suggests that the movement must be sluggish; but that there is a definite movement is shown by the fact that where there are a number of holes bored at intervals along the line of the "stream" and coloring matters are introduced into one of them, in a short time the color ap-

pears in the water coming from the adjacent holes in one direction but does not appear in the water from the holes in the opposite direction. But the average rate of movement has not been determined with a sufficient degree of accuracy to admit of its being stated. These currents are quite limited in their width; ranging in the cases tested, from a few feet to, in rare cases, more than 100 yards. And, as might be expected, the width is not at all constant, but while it gradually increases further down the "stream" as the supply of water becomes greater, yet this increase of width is by no means constant. The depth at which these underground water currents have been found varies from about 20 to nearly 100 feet, and generally they have been found at less than 50 feet below the surface.

The fact that in the case of some of these wells the water overflows at the surface is due to topographic rather than geologic influences. In some cases, especially at Charlotte, N. C., as mentioned in the table below, the flow from a single well amounts to as much as 10 gallons per minute. Here, as in other places where the overflow is slight—even less than one gallon per minute—the amount of water which can be pumped from such a well is considerably larger. Thus in the case mentioned at Charlotte (Latta Park) there are several overflowing wells with an average depth of 42 feet. The maximum natural flow from one of these wells is 10 gallons per minute, but with the application of a pump the eight wells yield readily 230,000 gallons per day. Again at Chester, S. C., one well which yields in natural overflow 6 gallons per minute, with the aid of a pump yields nearly 62 gallons per minute or 99,280 gallons per day. In another case, the maximum natural overflow of any one of the eight wells

bored at the Western Hospital, at Morganton, N. C., is only four gallons per minute, while the eight wells, with an average depth of about 39 feet, yield upon the application of a pump 165 gallons per minute or 237,600 gallons per day.

The quality of the water obtained from these wells has been pronounced satisfactory in every case by the health officials. Of course the continuation of this condition of things will depend largely upon the continued freedom from contaminating influences of these water basins, and one advantage of this system of water supply is that the basins, being generally limited in area, may be generally controlled by one or more individuals or a corporation, and may be thus kept free from sources of contamination.

AS might be expected, the search for the underground supplies of water has not by any means been successful in every case, but the limited experience leads one to believe that they may be found in a majority of communities, where search is extended over a sufficiently large area and is made with sufficient care. It would at present, however, be too much to claim that these underground supplies of drinking water can be found sufficient to meet all the demands of larger towns and cities, though they would prove of material service in this connection. But I anticipate that they will be found of greatest importance in connection with water supplies of smaller towns and of more or less isolated manufacturing establishments, where there are usually several hundred or several thousand operatives.

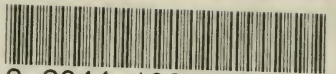
In the following tabular statement will be found a list of the more important places where these underground water currents have been found and where the gang well system has been introduced, the name of the

special establishments for which the wells were bored, the number of wells at each place, the average depth of the wells, the natural overflow in one minute of time from that one of the series of wells from which the overflow is largest, and the aggregate yield of water from the several wells at each place in 24 hours when the steam pump is applied. The data for this tabular statement has been supplied by Mr. Henry E. Knox Jr., of Charlotte, N. C., who bored all of these wells, and who states that out of 23 surveys made by him, only three were unsuccessful in locating the desired quantity and quality of water.

LIST OF FLOWING WELLS IN THE PIEDMONT PLATEAU REGION OF NORTH AND SOUTH CAROLINA.

BORED BY HENRY E. KNON, JR., HYDRAULIC ENGINEER, CHARLOTTE, N. C.

PLACE.	Average Depth in feet	Strata.	No. wells.	Max. flow per minute from one well.	Pumping capacity 24 hours.	For whom bored
Burlington, N. C.	27.5	Bed of gravel.	5	1 Gallon.	20,000 Gals.	Aurora Cotton Mills.
Morganton, "	28.3	Decom. gneiss	8	"	150,000 "	Burke Tanning Co.
"	39.0	"	8	"	237,600 "	State Hospital.
"	41.0	"	5	"	100,000 "	Deaf and Dumb School.
Rock Hill, S. C.	50.0	" granite	4	5	72,000 "	Winthrop N. and I. College.
Fort Mill, "	35.0	"	4	5	30,000 "	Fort Mill Man'f. Co.
Pelzer, "	21.0	" gneiss	4	10	100,000 "	Pelzer "
"	38.0	"	5	1	100,000 "	" "
Chester, "	40.3	" granite	1	6	99,280 "	Gingham Mills.
"	42.5	"	1	2	30,000 "	" "
"	72.0	"	2	1	30,000 "	Catawba "
Charlotte, N. C.	42.0	"	10	10	230,000 "	E. D. Latta.
"	51.5	"	10	2½	200,000 "	Water Works Co.
Jonesboro, "	31.0	" schist	1	1½	5,000 "	Jonesboro Cotton Mills.
Reidsville, "	28.0	" granite	10	1	100,000 "	Edna Cotton Mills.



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