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JOURNAL  
OF THE  
Elisha Mitchell Scientific Society.

NOTES ON THE FOREST RESOURCES OF  
NORTH CAROLINA.

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BY W. W. ASHE.

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BOTANIC DIVISIONS.

North Carolina can be divided topographically into three fairly well-marked divisions:

1. An eastern or coastal plain region, extending inland from the coast a distance of one hundred to one hundred and fifty miles and having an aggregate area approximating 24,000 square miles. Its surface is that of a gently undulating plain of less elevation (ten to twenty feet above sea-level) and a more nearly level surface eastward, and becoming more elevated (three hundred to five hundred feet) and rolling along its western border. Its soil is generally a sandy loam or sand, though in limited areas clay predominates. In the more eastern portion of this region are numerous extensive swamps or marsh areas surrounding small lakes or bordering the streams. In some of these the soil is mainly an admixture of sand and vegetable mold, while in others it is a fertile loam. In this district the normal annual temperature is about  $61^{\circ}$  F., and the normal annual rain-fall about fifty-five inches.

2. A middle district, which extends westward to the Blue Ridge, two hundred miles beyond the coastal plain, and extends across the State parallel to it, having an area of about 22,000 square miles. In the east it is rolling, but towards the western border is rugged and hilly, and in places even mountainous, being penetrated by mountain spurs from the Blue Ridge. It has an average altitude of eight hundred and fifty to nine hundred feet, but rises at its highest peaks to a little over 3,000 feet, while along its extreme eastern border it is not over four hundred to five hundred feet. On the uplands the soil may be classed in general terms as a loam, which becomes sandy in some places and clayey in others. Along the streams there is usually a rich, dark-colored loam with an admixture of humus. This region has an average temperature of about  $58.5^{\circ}$  or  $59^{\circ}$  F., and an annual rain-fall of about fifty inches.

3. The western district is an elevated, mountainous region, with an average altitude of 3,500 feet, but rising (at Mt. Mitchell) to 6,711 feet. This region includes the Blue Ridge, which forms its general eastern boundary, and the Great Smoky Mountains, which border it on the west. Numerous cross ridges, separated by irregular valleys, connect these two mountain ranges. The area of the region is about 6,000 square miles. Though the mountain slopes are often steep, and the valleys quite narrow, the soil is exceedingly fertile, being a loam generally rich in organic matter. The average temperature for the counties of this western district probably approximate  $50^{\circ}$  F., varying from  $57.8^{\circ}$  at Hot Springs to an estimated temperature for the top of Mt. Mitchell of less than  $38^{\circ}$ ,\* and the normal annual precipitation is about fifty-seven inches.

There are three fairly well-marked botanic divisions coin-

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\**Climatology of North Carolina*—N. C. Agr. Exp. Sta. Report. Raleigh, 1892; p. 166.

ciding in general with these topographic districts. The lower botanic division, however, extends a few miles west of the sandy coastal plain boundary line, and the third botanic division begins in the damp "coves" and the higher mountain spurs lying just east and south-east of the Blue Ridge.

It must not be inferred from the above statement that these botanic divisions are separated by any sharp lines on the two sides of which radically different conditions of soil and climate and vegetation exist, for while there are certain places where these conditions do change abruptly, generally such is not the case; but, on the contrary, these divisions are separated by what may be called transition zones, in which the conditions of the two adjacent regions commingle to a greater or less degree. Thus in the following counties we find transition conditions between the eastern and middle districts: Northampton, Warren, Vance, Franklin, Durham, Wake, Chatham, Moore, Montgomery, Richmond and Anson. And the tier of counties just east of the Blue Ridge may be regarded as the transition zone between the western and middle botanic districts. Here in the valleys we find physical conditions and plants such as characterize the middle district, and on the slopes of the higher ridges are found a climate and vegetation much like those of the mountain district.

These differences in topography and elevation, with accompanying differences in soil, corresponding in a general way to geological formations, have given this State a wonderful variety of woods, and have placed in juxtaposition trees normally separated by many degrees of latitude. Thus are found in North Carolina eight species of pines out of the thirteen given in the Tenth United States Census Report as occurring in the United States east of the Mississippi River; twenty oaks out of twenty-three; all of the six maples; three elms out of four; all seven magnolias;

five hickories out of eight, and four out of the six species of ash.

EASTERN DISTRICT.—The eastern or lower district, having its climate tempered by the near approach of the gulf-stream, has a decided southern or subtropical flora, as pronounced in the larger forest growth as among minor plants. The trees confined to this district, or but slightly entering the others, are: *Magnolia grandiflora* L.\* (Magnolia); *M. glauca* L. (Sweet Bay); *Prunus Caroliniana* Ait. (Mock Orange); *Bumelia lycioides* Gært.; *Gordonia Lasianthus* L. (Bull Bay); *Nyssa aquatica* L. (Black Gum); *N. uniflora* Walt. (Tupelo Gum); *Tilia pubescens* Ait. (Linn.); *Carya aquatica* Nutt.; *Planera aquatica* Gmel. (Planer Tree); *Quercus laurifolia* Michx. (Laurel Oak); *Q. cinera* Michx. (High Ground Willow Oak); *Q. virens* Ait. (Live Oak); *Q. aquatica* Walter (Water Oak); *Q. Catesbæi* Michx. (Turkey Oak); *Q. macrocarpa* Michx. (Mossy Cup Oak); *Q. lyrata* Walt. (Over Cup Oak); *Q. Michauxii* Nutt. (Swamp White Oak); *Pinus Australis* Michx. (Long-leaved Pine); *P. Taeda* Linn. (Rosemary, Loblolly, or Short-leaved Pine); *P. serotina* Michx. (Pond Pine or Savannah Pine); *Chamæcyparis spheroides* Spach. (Juniper or White Cedar); *Taxodium distichum* Rich. (Cypress); *Sabal Palmetto* Todd. (Palmetto).

MIDDLE DISTRICT.—In the middle section the prevailing growth is the hickories, oaks, elms, and short-leaved pines, common to all the Atlantic States, and these extend into the other sections and enter largely into the composition of their forests. The common trees through this district are *Magnolia umbrella* Lam. (Umbrella Tree); *Asimina triloba* Dunal. (Papaw); *Liriodendron Tulipifera* L. (Yellow Poplar); *Amelanchier Canadensis* L. (Sarvice);

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\*The names used in this paper are, with few exceptions, those given in Curtis' *Woody Plants of North Carolina*; Raleigh, 1860.

*Cornus florida* L. (Dogwood); *Gleditschia triacanthos* L. (Honey Locust); *Acer dasycarpum* Ehrh. (Silver Maple); *A. rubrum* L. (Red or Swamp Maple); *Negundo aceroides* Mœnch. (Box Elder); *Ilex opaca* Ait. (Holly); *Oxydendrum arboreum* D. C. (Sour Wood); *Nyssa multiflora* Wang. (Black Gum); *Diospyrus Virginiana* L. (Persimmon); *Fraxinus Americana* L. (White Ash); *F. pubescens* Lam. (Red Ash); *F. viridis* Michx. (Green Ash); *Sassafras officinale* Nees. (Sassafras); *Platanus occidentalis* L. (Sycamore); *Ulmus fulva* Michx. (Slippery Elm); *U. Americana* L. (Elm); *U. alata* Michx. (Winged Elm or Wahoo); *Carya alba* Nutt. (Shell-bark Hickory); *C. tomentosa* Nutt. (Hickory); *C. glabra* Torr. (Pig Nut); *C. microcarpa* Nutt.; *Juglans nigra* L. (Black Walnut); *Quercus phellos* L. (Willow Oak); *Q. nigra* L. (Black Jack); *Q. tinctoria* Barr. (Black Oak); *Q. coccinea* Wang. (Scarlet Oak); *Q. falcata* Michx. (Spanish Oak); *Q. obtusiloba* Michx. (Post Oak); *Q. alba* L. (White Oak); *Fagus ferruginea* Ait. (Beech); *Carpinus Americana* Michx. (Hornbeam); *Ostrya Virginica* Willd. (Iron Wood, Hop Hornbeam or Water Beech); *Betula nigra* L. (Black Birch); *Salix nigra* Mars. (Willow); *Populus angulata* Ait. (Cotton Wood); *P. heterophylla* L., *P. monilifera* Ait., *Pinus mitis* Michx. (Short-leaved Pine); *P. rigida* Mill. (Pitch Pine); *Juniperus Virginiana* L. (Red Cedar).

MOUNTAIN DISTRICT.—In this district occur, as characteristic forest trees: *Magnolia acuminata* L. (Cucumber); *M. macrophylla* Michx. (Magnolia); *M. Frazeri* Walt. (Wahoo); *Prunus serotina* Ehrh. (Wild Cherry); *Robinia Pseudacacia* L. (Locust); *R. viscosa* Vent. (Clammy Locust); *Cladrastis tinctoria* Raf. (Yellow Wood); *Ilex monticola* Gray; *Fraxinus Americana* Linn. (White Ash); *Æsculus flava* Ait. (Buckeye); *Tilia Americana* L. (Linn.); *T. heterophylla* Vent. (Linn.); *Halesia tetraptera* L. (Snow-drop Tree); *Stuartia pentagyna* L'Her.; *Betula lutea* Michx.

(Yellow Birch); *B. lenta* L. (Sweet Birch); *Quercus imbricaria* Michx. (Water Oak); *Q. rubra* L. (Red Oak); *Q. prinus* L. (Chestnut Oak); *Castanea vesca* L. (Chestnut); *Populus grandidentata* Michx. (Aspen); *Pinus pungens* Michx. (Table Mountain Pine); *P. Strobus* L. (White Pine); *Abies Fraseri* Lindl. (Balsam Fir or She Balsam); *Tsuga Canadensis* Carr. (Hemlock); *T. Caroliniana* Engel. (Hemlock); *Picea nigra* Link. (Black Spruce or He Balsam).

In addition to the above there are to be found in one or more of the botanical divisions of the State over two hundred minor trees, shrubs and vines of more or less value for fruit culture or floriculture, etc. There are four species of grape (*Vitis aestivalis*, *V. labrusca*, *V. vulpina*, *V. cordifolia*), from the first three of which cultivated varieties have sprung. There are also found in these several sections of the State several hundred herbs, various parts of which are extensively used for medicinal purposes, a discussion of the more important of which will appear in a future number of the JOURNAL.

#### ECONOMIC WOODS.

In the above statement a small number of the trees named as occurring in the different regions have timber of but little value, owing to a lack of strength and durability, and are of such small size as to have little economic value, and there are a few others of such infrequent occurrence as to be commercially unimportant. But in each region there are many valuable forest trees, and the following notes will contain a brief statement of their distribution, abundance, size, and uses:

*Magnolia acuminata* L. (Cucumber): Two to four feet in diameter, eighty to one hundred and twenty feet high. Frequent in the upper district with Yellow Poplar. Not over 5,000,000 feet standing in the fifteen counties through which its distribution extends. Has the same use as Yellow Poplar.

*M. Fraseri* Walt. (Wahoo) is a small tree, one to two feet in diameter. Very common in western district; used medicinally, rarely for lumber; very ornamental.

*Liriodendron Tulipifera* L. (Yellow Poplar): Four to eight feet in diameter, one hundred to one hundred and twenty feet high. Occurs in all districts; very common in western. Lumber is used in building very extensively, for interior wood-work and cheap furniture. The chief bodies standing are in Watauga, Yancey, Mitchell, Swain, northern Graham, Macon, Jackson, Transylvania, Wilkes and Alleghany. Altogether there is 50,000,000 feet of poplar lumber in these counties. The trees have been removed adjacent to the large rivers and around towns, as it is the building material of this section. Still abundant in the western tier of the midland counties, except along the railroads.

*Tilia Americana* L. (Linn.): A middle-sized tree, frequent in the higher mountains and mixed with *T. heterophylla* Vent. (Linn.), which is very common throughout the mountains, except around thick settlements, where it has been cut in winter, so cattle could feed upon its buds. Very abundant in Swain, Jackson, Macon, Transylvania, Yancey, Mitchell, Watauga and Ashe. The wood is light, soft and white; rarely sawn for ceiling. It is useful for making paper.

*T. pubescens* Ait. (Linn.): Very frequent in rich alluvial places along the coast. Same uses and character as the above species, but smaller.

*Æsculus flava* Ait. (Buckeye): Very abundant as a large tree on damp soil throughout the mountain district. It is not used commercially except around Bryson City, Swain county, where it is manufactured into excelsior.

*Acer saccharinum* Wang. (Sugar Maple or Sugar Tree): Very common throughout all mountain counties, where it reaches a height of ninety to one hundred feet and a diame-

ter of three to four feet; and it is found also in the swamps of Pender and Onslow and in low grounds of other eastern counties. It has been cut to a small extent for flooring and furniture, and in the northern counties small quantities of sugar are made from the sap.

*A. dasycarpum Ehrh.* (White or Silver Maple): A small tree, rarely more than two feet in diameter, sparsely distributed in all portions of the State, usually in moist places; more abundant in the mountain counties.

*A. rubrum L.* (Red or Swamp Maple): Tree two to three feet through and rarely sawn, and then for ceiling; abundant, especially in moist places, in all portions of the State.

*Robinia Pseudacacia L.* (Yellow Locust): Once very common through the mountain counties, though it has been very largely used up for posts in thickly settled regions. It is still widely distributed and abundant in Rutherford, Polk and other south-western counties, and occurs sparingly in the middle district. In Haywood and Swain there are factories making from it insulating pins for telegraph poles. The trees are one and one-half to two and one-half feet in diameter; sixty to eighty feet high. The wood is yellow, hard, and resists exposure and decay.

*Cladrastis tinctoria Raf.* (Yellow Wood): A small tree, one and one-half feet in diameter; forty to sixty feet high, with a deep yellow hard wood; it is mostly confined to rich "coves" of Graham, Macon, Clay and Cherokee counties, but is very frequent through these. It has been used in Cherokee county for making furniture.

*Prunus serotina Ehrh.* (Wild Cherry): Occurs all over the State, but only in the mountain counties does it reach sufficient size and abundance to become a valuable timber tree. There in rich, cold "coves" it becomes a tree two to four feet in diameter and eighty to one hundred feet high. It is a fine-grained, medium hard, red wood, taking a fine

polish; largely used for furniture and interior work of all kinds, and is one of the first trees removed, when easily accessible, on account of its high value. Large quantities of it still remain in certain regions, as in the north-western part of Ashe county and around Grandfather, Beech and Roan mountains. About the head-waters of Caney river there are probably 1,000,000 feet standing; in north Swain, especially on Ocona-Lufty River, about 3,000,000 to 4,000,000 feet; small quantities are found in other mountain regions; and in the north "coves" of the east slope of the Blue Ridge there is still some cherry timber remaining.

*Amelanchier Canadensis* L. (Sarvice): Occurs abundantly in the mountains, where it is a small tree, and is used there in turneries in some of the towns.

*Hamamelis Virginica* L. (Witch Hazel): A shrub or small tree, very common throughout the middle and upper districts. It is use medicinally.

*Liquidambar Styracifolia* L. (Red or Sweet Gum) is common throughout the middle and lower districts, becoming in the swamps and low grounds of the latter a very large tree, four to five feet in diameter and ninety to one hundred feet high. It forms with cypress and black gum about one-half of the growth of the deeper swamps in many portions of the eastern counties, and has been cut out in only a few places, as around Bladenboro, Wilmington, Newbern, Goldsboro, Hub, and in limited portions of Northampton, Perquimans, Pasquotank and Camden counties. The wood is hard and heavy, fine-grained, red; used for furniture.

*Cornus florida* L. (Dogwood) is common over the whole State. It is a small tree, with hard, compact, white wood; has been largely removed in many portions of the middle district, around larger towns, for shuttle-blocks, etc.

*Nyssa multiflora* Wang. (Black Gum): A middle-sized tree, found all over the State, in all soils. Its wood is very compact, with fibers interwoven, and is rarely used, except occasionally for hubs, mallets, etc.

*N. aquatica* L. (Black Gum) is a very large tree, four to five feet in diameter, common throughout deep swamps of the lower district. The wood and its uses are much the same as *N. multiflora*.

*Nyssa uniflora* Walt. (Tupelo Gum): A medium-sized tree, common in deep swamps in the section along and south of Neuse river. Its wood is very light, white, but with fibers interwoven as in the other species, and hence is very difficult to split, tasteless; used for wooden-ware of all kinds. Very little has been removed and only in a few counties.

*Oxydendrum arboreum* D. C. (Sour Wood) is a small tree, very common through mountains and the middle district. Its wood is firm, fine-grained and of reddish color, and is being used for making certain parts of furniture—chair rounds and legs, newel posts, balisters, etc.

*Kalmia latifolia* L. (Ivy): A large shrub, very common in mountains, growing generally in dense thickets; its matted roots, forming large “stools or burls,” are gotten out around Cranberry, Elk Park, Magnetic City, and in several counties south of the French Broad river, and used for making tobacco pipes, handles, etc., and the branches are used for rustic furniture. The wood is hard and fine-grained.

*Ilex opaca* Ait. (Holly) is a small tree one to two and one-half feet in diameter; common in wet, sandy soils of lower district, but found also in the other districts. The wood is very fine-grained and white; it has been largely removed in the north-east counties, but has not been touched in the south-eastern counties.

*Diospyros Virginiana* L. (Persimmon): A small tree with very hard, tough wood. It is common through the eastern and middle counties, but has been largely removed from Wilkes, Surry, Caldwell, McDowell, Lincoln, Catawba, Guilford, Forsyth and Union counties, being used in the manufacture of shuttle-blocks.

*Fraxinus Americana* L. (White Ash) was once common in wet or damp places over the entire State. A large tree two to four feet in diameter and eighty to one hundred feet high. Its wood is white, very elastic, and strong; and in the western counties it is used for making wagons, furniture, and especially the curled wood. In the eastern counties it is used for oars, barrel heads, and lumber. In the middle district it is used for making paper and lumber and furniture. It has largely been removed from the following mountain counties: Ashe, west Yancey, south Madison, Buncombe, Haywood, north Jackson and north Macon, Graham (except along Tuskegee creek), Cherokee and Henderson. Has been removed in middle district when accessible to railroads and larger streams.

*F. platycarpa* Michx. (Water Ash) is abundant in many of the larger swamps of lower district, to which it is confined. The counties of Pender, Sampson, Hyde and Pamlico still have very large bodies, but it has been removed where turpentine orchards have been worked.

*F. viridis* Michx. (Green Ash) and *F. pubescens* Lam. (Red Ash) are middle-sized trees, found only in middle district and used for lumber and making paper. Along lines of transportation they have been largely removed, but in inaccessible places they are still abundant.

*Carya alba* Nutt. (Shag-bark Hickory) is frequent in the middle and upper districts.

*C. amara* Nutt. (Bitter-nut Hickory) is common in wet places in the upper districts.

*C. glabra* Torr. (Pig-nut Hickory) abounds in dry soils in all portions of the State.

*C. tomentosa* Nutt. (Common Hickory) is very common in dry soils through the lower and middle districts.

All of these hickories have been cut away, more or less, around towns for fire-wood, and for the manufacture of spokes, handles, and wagon material, especially around large towns in the middle district.

*Juglans nigra* L. (Black Walnut) is largely removed in all mountain counties, except Wilkes and Madison and in a few other counties where it has been especially preserved on limited areas; and in neither of these counties is it very abundant, though there are many trees of large size. It is also found occasionally in many counties of the middle and lower districts, at a distance from means of transportation, but it is there a tree of medium size.

*J. cinera* L. (Butter Nut) is frequent in most mountain counties and extends but a short distance below the mountains. The curly wood is used for furniture and interior finish.

*Quercus alba* L. (White Oak) and *Q. obtusiloba* Michx. (Post Oak) are common over the whole State except in the extreme east, although they have been largely removed in middle district for fuel, cross-ties, wagon material, staves and lumber. But large quantities yet remain, and a vigorous second growth of equal density and strength to the original is coming on, so that it appears that there will be an abundance of both at all times over the larger part of the State.

*Q. tinctoria* Bartr. (Black Oak), *Q. coccinea* Wang. (Scarlet Oak), and *Q. falcata* Michx. (Spanish Oak) are all most abundant in the middle district on dry soil. They are generally not used where good white oak can be obtained; rarely used for staves and wagon material; more frequently for fence rails, furniture and clap-boards.

*Q. macrocarpa* Michx. (Mossy-cup Oak), *Q. lyrata* Walt. (Over-cup Oak), and *Q. michauxii* Nutt. (Swamp White Oak) all occur in swamps of the eastern section, and where contiguous to large turpentine orchards have been used for staves, and they are also used to some extent for rails, clap-boards, etc.

*Q. laurifolia* Michx. (Laurel Oak) and *Q. aquatica* Cates. (Water Oak) are trees still very common in lower districts,

where they are rarely used, except for rails, the timber being open and porous.

*Q. Rubra L.* (Red Oak) occurs in the cool, fertile soils of the middle and mountain districts, and sparingly in the eastern counties. It reaches, under favorable conditions, a diameter of four feet and a height of seventy to eighty feet; the wood is reddish, open, and rather coarse grain, but strong, and is used extensively for clap-boards, cooperage, and articles of furniture.

*Q. imbricaria Michx.* (Water Oak, Laurel Oak or Shingle Oak) is infrequent, occurring only in counties west of the Blue Ridge; a medium size tree, with rather open, porous wood, rarely used, where better material can be obtained, for clap-boards, staves, etc.

*Q. Prinus L.* (Chestnut Oak) is common on dry ridges through mountain and more elevated parts of the middle section. It is used for furniture, wagon material, and the bark is used for tanning. It has been largely removed around Cranbury, Asheville and Morganton.

*Castanea vesca L.* (Chestnut) is very abundant through all mountain regions and is found sparingly in some of the Piedmont counties, though the best trees have in many places been removed for rails. It is sawn for lumber at Dillsboro and Asheville, and has been removed largely from Graham, Ashe and Buncombe counties.

*Populus grandidentata Michx.* (Poplar), *P. heterophylla L.* (Cotton Wood), *P. angulata Ait.* (Cotton Wood), and *P. monilifera L.* (Cotton Wood): All except the first occur frequently in lower or middle districts, though in the neighborhood of turpentine orchards they have been used for making barrel heads. The first named species is confined to the upper part of the middle district.

Of the eight pines occurring in this State five are of the first economic importance. They are *Pinus Strobus L.* (White Pine), *P. australis Michx.* (Long-leaved Pine),

*P. Taeda L.* (Short-leaved or Old Field Pine), *P. rigida Mill.* (Black Pine), and *P. mitis Michx.* (Short-leaved or Yellow Pine). *P. scrotina Michx.* is very rarely used. *P. pungens* and *P. inops Ait* are practically worthless for timber purposes.

*P. Strobus L.* (White Pine) extends in a narrow belt along the Blue Ridge from southern Ashe to Macon, also occurs in Graham, north Haywood, and adjacent parts of Madison, and in northern Madison and western Mitchell. It is locally used for shingles. Has been removed only around Marion, in parts of Jackson, Transylvania and Macon counties.

*P. australis Michx.* (Long-leaved or Turpentine Pine) extends over a large part of the sandy land of the lower district, but occurs only sparingly north of Roanoke river and west of Wake and Richmond counties. It formerly existed as a pure forest over the sandy lands of this area. But the inroads which have been made through it for the past century to supply naval store products, ship timber and building material have removed or destroyed most of the forest adjacent to the railroads and immediately along the larger water courses. The largest bodies still standing are in Montgomery, Sampson, Robeson, Harnett, Cumberland, Johnston and Richmond counties. Large bodies of virgin pine forest are rare except along the extreme western border of the pine belt.

*P. Taeda L.* (Rosemary, Loblolly, Short-leaved or Old Field Pine) is found over the whole of the eastern district, but growing originally on wet clay lands and often forming considerable clumps in small swamps. When the long-leaved pine is removed this species takes its place on the sandy land and is there called old field pine. In its original growth in swampy places it is decidedly the largest pine in the State, having a height of one hundred to one hundred and twenty feet and a diameter of from three to five feet. Here it has a fine, even grain, heart very large,

with but little resin, and a strong, durable wood. The high price paid for large stocks for ship material causes its removal where accessible, even in advance of *P. australis*; but it is still abundant where transportation facilities at present are not suitable for its removal. Its second growth on dry, sandy land is a smaller tree, sappy, with very coarse grain, and little or no heart, the wood decaying rapidly on exposure; but as it makes a beautiful wood for interior finish it is largely sawn around large towns and kiln-dried for that use. The general character of the trees growing on dry, sandy soils is so different from that of those growing about the wet lands that the two trees are usually (though erroneously) believed by lumbermen to belong to different species.

*P. serotina Michx.* is common over wet lands in the south-east counties and is sometimes sawn with *P. Taeda*; but the lumber is gummy and of poor quality.

*P. mitis Michx.* (Short-leaved or Yellow Pine), formerly common over the whole area of the middle district and extends through the southern part of the mountain district, being mixed with deciduous trees. It has been largely removed for lumber around the larger towns and thick settlements, and along the lines of the railways; and through Catawba, Lincoln and Gaston counties large quantities of it have been cut and used for making charcoal. Wilkes, Caldwell, Alexander and Rutherford counties contain the finest bodies of this timber to be found in the middle district. This tree frequently reaches two to three feet in diameter and seventy to eighty feet high.

*P. rigida Mill.* (Black or Pitch Pine) is a tree slightly smaller than the preceding and making inferior lumber, but largely used along with it. Surry, Wilkes, Caldwell, Burke, McDowell and Polk counties contain the larger part of what is known to occur east of the Blue Ridge; but there is also a great deal in the mountain counties south of the French Broad river.

*Tsuga Canadensis Carr.* (Hemlock) is a large tree; abundant in moist regions through nearly all of the mountain counties. It has only been removed in northern Mitchell, where it has been barked for tanning purposes, and along the Little Tennessee river.

*T. Caroliniana Engel.* (Hemlock) is frequent on ridges along the Blue Ridge from eastern Ashe to Macon. It has been cut in only a few localities, for frames for houses, etc.

*Picea nigra Link.* (Black Spruce or He Balsam) forms twenty square miles of virgin forest in Watauga, Mitchell, Yancey, Haywood and Swain counties. Has been cut only in some places about Roan mountain. It is a tree of three feet in diameter and sixty to ninety feet high.

*Abies Fraseri Lindl.* (Balsam, or She Balsam) covers the summit of the highest mountain peaks.

*Chamæcyparis sphaeroidea Spach.* (Juniper or White Cedar) occurs in many of the large swamps in the eastern district, especially in Harnett, Tyrrell, Gates and most of the other extreme eastern and north-eastern counties. It has been largely removed from Pasquotank, Perquimans and Camden counties, and about the larger eastern towns. It is a medium-sized tree and is very valuable for making pails, tanks, boats, shingles, etc., for which purposes it is largely used.

*Taxodium distichum Rich.* (Cypress) occurs abundantly in the swamps of the eastern section. It has been worked up around larger towns and in the north-eastern counties of Currituck, Perquimans, Hertford and Camden. It is a very large tree, four to five feet through and from eighty to more than one hundred feet high. Its wood is light, and is used largely for lumber, shingles and boats, and to a small extent for furniture.

*Sabal Palmetto Lodd.* (Palmetto) occurs somewhat abundantly on Smith's Island, at the mouth of the Cape Fear river. It is a small tree about one foot

in diameter and thirty or forty feet high. It has been found to serve an excellent purpose for piling, and this is about the only use to which it has been put.

*Juniperus Virginiana* L. (Red Cedar) is a common but rather small tree throughout the State, but most abundant in the south-eastern counties. It is used mainly for boxes and posts.

TRANSPORTATION FACILITIES.—Railroads penetrate the State in every direction, there being but few counties which are not touched by them. For marine shipment material from all north-eastern counties goes readily by way of Norfolk. For counties drained by the Tar and Neuse Newbern is the natural shipping point, while for the whole southern and central sections Wilmington is the central point, vessels drawing over twenty feet being able to enter its harbor.

ACCESSIBILITY OF EXISTING FORESTS.—While there is no large body of timber in the State valueless on account of its inaccessibility, there are many so situated that removal is not feasible with the existing means of transportation. But the experience of the past ten years is sufficient to prove that these large bodies of virgin forests to be found in the State will be penetrated by railroads in the near future, as the demand for the timber increases. The hard wood forests in some of the counties west of the Blue Ridge are naturally tributary to Tennessee, and the timber in the form of logs is being removed by floating down the creeks and rivers with the aid of flood dams. Many of these mountain streams are of sufficient size and rapidity to afford ample means for logging. East of the Blue Ridge tracts not adjacent to large streams or railroads are being reached by short timber roads. A number of such roads are now in operation and others are being constructed. In the eastern district, on pine lands where the country is flat, wooden and iron tramways are laid to be operated by horse-

power or narrow guage steam engines. In the eastern swamps, to get at the cypress, white cedar and other trees, the plan adopted by larger companies is to dig canals by hand or with dredges parallel to the drainage streams of the swamps. The logs are floated through these canals to some central point and there worked up.

#### FOREST MANAGEMENT.

Up to within the past few years forest management in North Carolina was deemed quite a useless business, but lately prudent individuals have placed large estates under foresters, one of whom was trained in European schools of forestry. As yet, however, this is little more than an experiment.

During the past two years the North Carolina Geological Survey has made a careful examination of the forests of the State with a view to the inauguration of modern methods of forest management, and the securing of such laws as will best encourage forest protection and improvement.

During the present year (1893) the Survey, recognizing the fact that the long-leaved pine (*P. palustris* Miller, or *P. australis* Michx.), a most valuable tree in this State, does not, under the existing conditions, extensively reproduce itself, has begun an examination of the causes operating against its increase and means by which it can be planted and economically cultivated, so as to make use of the waste lands formerly entirely occupied by this tree but now barren or covered with the loblolly pine (*Pinus Tadea* L.). Experiments are now under way for the purpose of determining the relative fertility of its seed as compared with those of other pines; causes why other species are so widely disseminated over cleared lands, while the long-leaved pine does not appear to be so; methods of planting, raising and protecting young pines; insects and fungous ene-

mies, and the damage done to the young pines by hogs, cattle, fires, etc.

#### WOOD-WORKING ESTABLISHMENTS.

A few facts, taken largely from the "Hand-Book" of North Carolina,\* concerning wood-working establishments should be stated in this connection. Although little of the lumber sawn in North Carolina, other than for buildings, is worked up in the State, yet the number of wood-working factories is constantly on the increase. The most numerous concerns are manufactories of carriages and buggies. "Of these Alamance county has two, Alexander two, Ashe one, Beaufort one, Bertie three, Caldwell one, Chatham one, Cleveland one, Cumberland two, Davidson two, Durham one, Forsyth six, Gates two, Guilford two, Haywood one, Halifax one, Hertford three, Lenoir two, Lincoln two, Moore two, Pasquotank one, Randolph two, Sampson two, Vance one, Wake one, Warren three, Washington three, Wilkes two, Wilson one, Yadkin four—in all fifty-eight, established in thirty out of the ninety-six counties of the State, and representing every section in it. Among them there is wide range of excellence, defined and governed largely by experience and time. Many of them are new, the product of the new industrial revolution. A few are old and are meritorious, not only for the character of the work done by them, but because of the courage and foresight which gave them existence far in advance of similar enterprises in the State.

"Not less important, and of much wider application, is the manufacture of wagons, carts, etc., conducted by thirty-two different establishments in almost the same number of counties, as follows: Alamance has one, Alexander two, Anson three, Cabarrus one, Caldwell one, Catawba one,

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\**Hand-Book of North Carolina*—Raleigh, 1893, pp. 273-275.

Clay one, Cleveland one, Cumberland two, Pamlico one, Pender one, Rutherford one, Surry one, Stanly one, Wake three, Yadkin one. One of the largest of these is at Waughtown, near Winston-Salem, founded in 1834. Another large one is at Hickory."

"Of furniture factories, there are twenty-five, of which one is in Ashe, three in Buncombe, one in Davie, two in Forsyth, one in Gaston, two in Guilford, one in Henderson, three in Lincoln, one in Macon, one in Martin, one in Mecklenburg, one in Montgomery, one in Moore, two in Rowan, one in Surry, one in Wake, one in Wayne, and one in Yadkin.

"For the making of hubs, spokes, and handles there are six factories, viz.: Bertie has one, Guilford one, Mecklenburg one, Montgomery one, Rowan one, Rutherford one.

"Of sash, door and blind factories there are twenty-four, viz.: Buncombe has two, Burke one, Cabarrus one, Caldwell one, Catawba two, Davidson two, Durham one, Forsyth one, Gaston one, Guilford three, Johnston one, Rowan three, Stanly one, Surry one, Wake two, Wilkes one.

"Of another variety of wood-working factories is that at Newbern for the manufacture of plates and dishes made out of sweet-gum, and also berry baskets.

"At Wilmington a somewhat similar establishment was operated by steam and employed one hundred and twenty-five people. The material chiefly used is gum logs, and the product is butter plates and baskets, berry baskets and crates.

"Of the other simpler and ruder establishments for the conversion of the product of the forest there are, as nearly as can be ascertained, in operation in the State one hundred and fourteen steam saw-mills, eighty turpentine distilleries (undoubtedly below the actual number); and, as largely connected with the products of the forest, a very large

number of tanneries, the best and largest equipped of which is the one at Morganton, constructed and conducted on the most advanced scientific application of theory to intelligent practice.

“In connection with paper manufacture it may be said that originally using only the waste of textile fabrics, the immensely increased consumption of paper demanded other raw material, for the supply of which human ingenuity was heavily taxed. The additional material has been found in wood-pulp, mechanically or chemically prepared. The abundance in North Carolina of soft woods suitable for such purposes has led largely to the combination of wood-pulp with cotton, flaxen and hempen fiber; and the factories now in operation in the State are able to supply as good a material for book, printing and wrapping paper as can be made elsewhere. There are three principal paper-mills in North Carolina—that at Salem, in Forsyth county, at Falls of the Neuse, in Wake county, and at Long Shoals, in Lincoln. The product of these mills is bristol-board, writing paper, book and newspaper, and wrapping paper of all kinds.”

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NOTE.—On page 6, six lines from the bottom, “approximate” should read approximates. And on page 11, eleven lines from the top, “50,000,000” should be 500,000,000.

## NOTES ON THE DEFLECTIVE EFFECT OF THE EARTH'S ROTATION AS SHOWN IN STREAMS.

BY COLLIER COBB.

So early as 1837, Poisson produced his general equations for determining the influence of the earth's attraction and rotation on the apparent motion of a projectile, and he applied them to the case of a material point constrained to move on a given curve and attached to the surface of the earth, omitting the effects of friction and the resistance of the air.

In 1859, Ferrel published in *Runkle's Mathematical Monthly* his celebrated paper on the *Motions of Fluids and Solids on the Earth's Surface*, in which he stated that, "In whatsoever direction a body moves on the surface of the earth, there is a force arising from the earth's rotation which deflects it to the right in the northern hemisphere, but to the left in the southern."

Karl E. von Baer, in a paper, *Ueber ein allgemeines Gesetz in der Gestaltung der Flussbetten*, published in the bulletin of the Imperial Academy of Sciences of St. Petersburg, in 1860, showed that the observed changes of position in streams might be explained as a consequence of the earth's rotation; yet the makers of our scientific textbooks have not taken the pains to give a correct, or rather, a complete, statement of the true value of this deflective force. Dana states it clearly and correctly in his *Manual of Geology*;<sup>\*</sup> but Geikie<sup>†</sup> speaks of it as an *easterly*, a *westerly* deflection, seeming to regard it as a getting left behind, and the same expression is used by Reclus<sup>‡</sup> in speaking of the rivers of Gers.

Von Baer's explanation does not account for the fact that

<sup>\*</sup> Third edition, p. 650. <sup>†</sup> Third edition, 1893, pp. 15, 16. <sup>‡</sup> *La France*, pp. 115, 116.

rivers flowing east or west have their banks worn away in the same manner as those flowing north or south. A body at rest upon the earth, and free to move in any direction upon it, "is maintained in equilibrium by attraction directed towards the earth's center, and centrifugal force directed away from the axis. If the centrifugal force ceased, the body would evidently move towards the nearest pole as down a hill. From the poles to the equator may therefore be regarded as uphill—bodies free to move being prevented from going down towards the poles by centrifugal force. Suppose now a body to move from west to east—that is, in the same direction as the earth revolves; the centrifugal force of the body is increased, and there is a tendency to move uphill towards the equator. If the motion be from east to west, the centrifugal force is diminished and the body tends towards the pole. In each case the tendency is towards the right in the northern hemisphere and towards the left in the southern."\*

Admitting the sufficiency of the terrestrial rotation for the deflection of streams, we must look for our examples to those regions where the strata are essentially horizontal and horizontally homogeneous. McGee, in his paper on the geology of the Chesapeake Bay, says: "It may be noted in passing that, throughout its gorge, the Susquehanna River hugs its left shore the more closely, and apropos to the hypothesis of the dextral deflection of rivers by terrestrial rotation (commonly known in Europe as Baer's law), specifically applied by Kerr to the water-ways of the Middle Atlantic slope, and recently discussed in more general terms by Gilbert, Davis, Hendricks, Bains, and others, it may be mentioned that the different water-ways of the Middle Atlantic slope are not only inconsistent in their behavior at and above the fall-line, but in many cases the same stream has not behaved uniformly since the excavation of its gorge was initiated."†

\* A. C. Bains, in a paper read before the Philosophical Institute of Canterbury, New Zealand, October 4, 1877.

† Seventh annual report of the Director of the United States Geological Survey, p. 554.

McGee's objection is done away with by the fact that the Susquehanna River is not situated in a region of the required horizontal homogeneity, and that if it now shows a preference for its left bank, that preference is probably an inheritance from the time when the favoring conditions did exist, before its superimposition upon the Wiconisco and Tuscarora-Mahanoy synclines, when the course of the river was the reverse of what it is now, and its present left bank was its right bank.\*

Turning now to the regions of horizontal homogeneity, we see that their streams all show this right or left deflection, according as they are north or south of the equator. Such a region is that where the phenomenon was first observed, in the middle and lower courses of the Volga. Here all of the conditions are most favorable; the river has a considerable length of course, and the mass of water is powerful enough to clear away any obstacles; "there are enormous floods which periodically increase the force of erosion in the currents, and the cliffs are composed of friable rocks."† Two centuries ago the principal mouth of the Volga flowed directly to the east of Astrakhan; since that time the great current has successively hollowed out for itself fresh beds, tending more and more to the right, and at the present day the branch navigated by vessels turns to the south-south-west. The Volga, up to its near approach to the sea, has a high right bank, and the erosion-valley, which slopes gently on the left, is bounded by rather abrupt cliffs on the right.

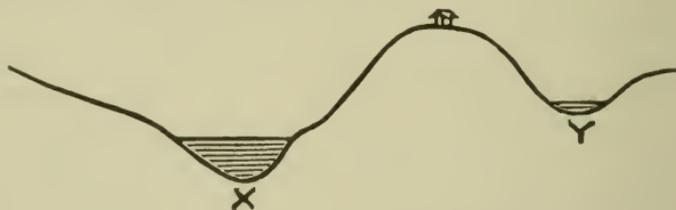


FIG. I.—THE VOLGA AND THE RWJAGA.

\* See Rivers and Valleys of Pennsylvania, W. M. Davis, *National Geographic Magazine*, Vol. I, p. 47, 1889.

† Von Baer.



Turning to the United States and selecting a few places where the necessary horizontal homogeneity is found, we have no trouble in pointing out examples. "The south side of the island of Long Island is a plain of remarkable evenness, descending with gentle inclination from the morainic ridge of the interior to the Atlantic Ocean. It is crossed by a great number of small streams which have excavated shallow valleys in the homogeneous modified drift of the plain. Each of these little valleys is limited on the west or right side by a bluff from ten to twenty feet high, while its general slope on the left side merges imperceptibly with the general plain. The stream in each case follows closely the bluff at the right."\*

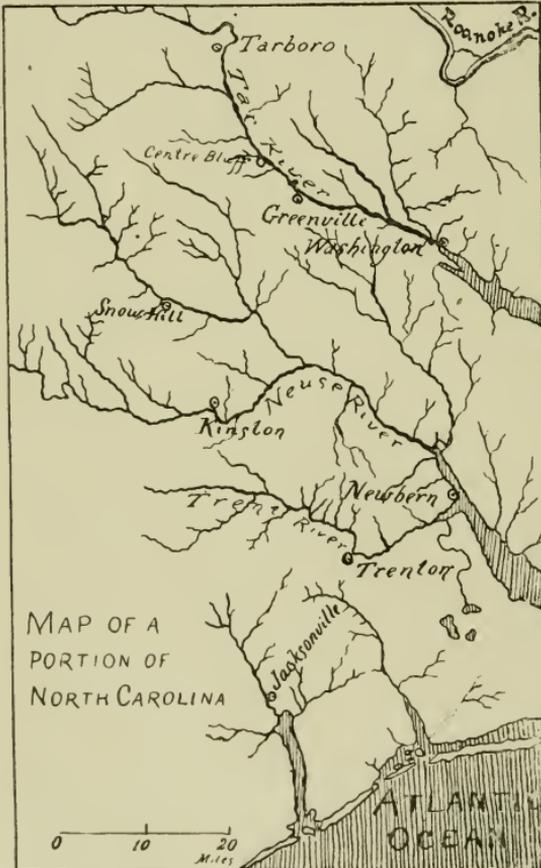


FIG. III.

The peculiar topography of the eastern portion of the Carolinas, where the necessary conditions exist, has been pointed out by Tuomey and by Kerr. Here the streams have cut through the Quaternary and Tertiary formations, and well into the Cretaceous, and in every instance they present the high right bank, with the low sloping country on the left; and, as may be seen by the sketch-map, the tributaries of the Roanoke, the Tar,

\* G. K. Gilbert, *Am. Jour. Sci.* 3d xxvii. 431.

the Neuse, and the Cape Fear run well back to the streams lying to the northward. In the case of these streams the dip of the strata is not such as to aid in the making of the right bank higher. Such conditions are represented in Fig-



FIG. IV.



FIG. V.



FIG. VI.

ure IV. In Figure V the arrangement of the strata is such as to hinder rather than help the deflective effect of rotation; and yet this is the structure of the Carolina region, as shown in Figure VI, which is taken from Kerr.\* But the rocks here are imperfectly lithified, and so friable as to yield readily to the influence.

The Mississippi River does not act consistently throughout its course, but in most instances its right bank is higher except where the prevailing winds are from the north-west. At Burlington, Iowa, the east or left side is low, and the trains of the C., B. & Q. Railroad reach the bridge over embankments and trestle-work, but run directly into the town on the high right bank of the river. At Dubuque just the opposite conditions exist.

Turning to regions south of the equator, we find in the plains of Canterbury, New Zealand, the requisite conditions. The Rakaia River cuts through Quaternary strata and into late Tertiary, and its left bank is its steeper bank. This is also shown in all the rivers entering Tasman Bay through strata of the same age, and there are doubtless many other cases in the same region. I have not at hand the maps and geological report for that region.

\* Geology of North Carolina, Vol. I, 1875, p. 10.

Those who are familiar with the map of South America, where the older rocks have been decomposed for great depths *in situ*, and where the younger rocks are but imperfectly lithified over great areas, must recall the fact that nearly all the streams have their longer tributaries on the right, showing a left-hand deflection of the main streams.

The cases cited serve my purpose of showing that wherever the conditions permit the influence of the earth's rotation is perceptible.

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## THE STONE ARCH.

BY WILLIAM CAIN, C. E.

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The theory of the voussoir arch has long exercised the ingenuity of mathematicians, and it may prove interesting, before giving the results of some recent investigations by the writer, to give brief statements of some of the leading theories that have been proposed, from time to time, as indicating the path followed in such original investigations.

As we should naturally expect, the theories proceed from the simplest, where the arch is assimilated in its action to a wedge, to the most complex, where the deformation of each individual stone under stress is considered.

In most of the theories hitherto proposed the arch is regarded as inelastic and the stones infinitely strong, so that the resultant thrust of one part of the arch against another can take place along the very edge of a joint without crushing ensuing.

These simple hypotheses unfortunately do not express the actual conditions, which involve the consideration of the elasticity of all the materials entering into the construction of the arch, the fit of the stones, thickness and

degree of hardness of the mortar joints (if any), settlement and time of striking of the centers, the manner in which the loads are transmitted to the arch ring, the relative density of the various stones, and finally the dynamic effect of moving loads. The true conditions are thus seen to be so complex as to make the true solution of the stone arch one of the most difficult, if not the most difficult, in all the range of the application of the laws of mechanics to engineering structures.

The latest theory, given further on, includes the most essential of the conditions just outlined, but not all of them; so that it is not proposed as a final and complete solution of the problem, but as one sufficiently near to make the results of decided practical value, approximating to the exact truth, as the hypotheses are more nearly realized in the construction of the arch ring.

Recurring now to earlier theories of the arch, Lahire, at the beginning of the last century, considered that the arch would break along "joints of rupture," half way between the crown and the springing, and he assimilated the action of the upper part to that of a solid wedge, tending to slide downwards along the joints of rupture, which last were considered perfectly smooth, so that the pressure there was directed normally to the point.

This very crude hypothesis was adopted by Eytelwein, who, however, found that joint of rupture for which the pressure exercised against an abutment was a maximum. As a matter of fact, friction can be exercised at any plane joint, which Eytelwein only imperfectly considers; but admitting it, the direction of the thrust at any joint of rupture becomes indeterminate, so that apart from other defects, the theory gives no definite solution.

Coulomb, in 1773, made a great advance by considering that an arch could not only fail by *sliding* along some joint, but also by *rotation* along the edges of certain joints.

He assumed the horizontal thrust at the crown always to pass through either the upper or the lower edge of the joint and found its minimum value, *so that no rotation would occur* about the lower or upper edge of any joint below the crown and such that no sliding could occur along any joint.

It is not necessary to explain the ingenious method by which the true thrust, after his theory, was ascertained. The theory was a marked improvement over the wedge theory, and it has been followed by a host of authors, with various improvements, even up to the present day.

As the thrust either at the crown joint or the lower joints of rupture cannot act along an edge without crushing ensuing, it is evident that the true positions of the thrusts at these critical joints has not been correctly ascertained; further, there is nothing in the theory to raise the indetermination.

The next advance in the theory was made by certain authors who used a *funicular polygon* in studying the resistance at the various points, a method which is still the basis for the analytical treatment of the arch.

It required but an additional step to see that *the curve connecting the centers of pressure* on every joint of the arch ring (to which the proper "funicular polygon" approximates for segmental arches) was a surer test of the stability of an arch ring and that, *in a stable arch*, it must always be possible to draw some "curve of resistance" (as the curve connecting the centers of pressure is called) within the limits of the arch ring, or, for safety, within much narrower limits.

The exact location of this curve, for any arch, loaded in any manner, will completely solve the problem for that arch; but where an infinite number of possible curves of resistance can be drawn within the arch ring (or narrower limits), all varying in the point of application, direction or

intensity of the thrust at the crown, it is evident that some additional principle must be introduced to enable us to choose the true one. Mosely introduced for this purpose *the principle of the least resistance*, which at once fixed the true curve as the one corresponding to the minimum horizontal thrust. This caused the results to agree with those of Coulomb, in most cases, though not in all, as the curve so determined does not, for some arches, pass through either edge of the crown joint, as Coulomb's theory requires.

In this and previous theories the arch and load were taken as symmetrical with respect to the vertical through the crown which thus restricts the theory to structures having fixed loads and rendering it of little service in the investigation of the strength and stability of road or railroad arch bridges subjected to a moving load, which produces a maximum distortion when placed over one haunch of the arch; further, the theories demanded incompressible voussoirs of infinite strength, which do not exist.

Scheffler developed very completely the theory of curves of resistance for the least horizontal thrust, for both symmetrical and unsymmetrical arches and loading; but as his theory requires the thrusts at the critical joints to pass through the very edges, it cannot apply to ordinary stones, where crushing would result, as a matter of course. Now, as crushing does not occur at the joints in well-designed arches, it follows (without other considerations) that Scheffler's theory must, at least, be modified. The writer did this in introducing the theory to American readers in 1874, by empirically limiting the curve of resistance to the middle third of the arch ring. With such a restriction, for a joint with mortar, there would be no tension exerted anywhere along the joint, and for a joint without mortar there would be a compression throughout the whole length of the joint, so that no joint would open. Such restrictions had already been suggested by Rankine, Woodbury

and others, as leading to safer results in proportioning an arch. The writer, however, called attention to the fact that, as in most well-built arches, the joints did not open, therefore, by experiment on a big scale, it was shown that the true curve of resistance in arches, as generally built, did not leave the middle third; hence, for usual depths of key-stone and usual loads, the true curve of resistance was found somewhere in the middle third. Its position in the middle third of the arch ring could be provisionally found by the principle of least resistance, though it was admitted that its exact position was dependent on the deformation of the arch ring under stress, due to its elasticity, the laws of which were not known at the time.

However, after mathematicians had developed a true theory of the *solid elastic arch*, "fixed at the ends" in position and direction, it seemed possible to apply it to the voussoir arch, and thus locate accurately the true curve of resistance, provided the following conditions were fulfilled:

1. No mortar was to be allowed between the arch stones or voussoirs;

2. The arch stones must be cut so perfectly that they will fit exactly, when not under stress, in place on the "center"—supposed unyielding;

3. Under these circumstances the curve of resistance, determined after the theory of the solid arch for the full sections of the arch ring, must lie in its middle third. If this last condition does not obtain, the solution is still possible, though the full sections cannot be used at certain joints, which involves a tentative method of finding the parts of the joints under stress and the resulting resistance curve, which makes a practical solution of the case much more difficult.

Under the conditions assumed above the deformation of the voussoir arch is exactly that of the solid arch and there can be no question as to the theory applying.

It is admitted, however, that it is difficult to cut the stones with the exactness demanded, and in addition, there will be a slight yielding of the centers, though the stones can easily be cut to bear along the whole length of joint when placed in position on the centers after they have yielded somewhat, as it only requires a close fit of the key-stone after the other stones are in place.

If thin cement mortar joints be used, that are allowed to harden perfectly before the centers are removed, the arch ring is assimilated completely to a solid arch, except that in the theory the successive blocks of cement and arch stones with their different moduli of elasticity must be considered, making the solution very complex. It would seem though that for very thin joints the theory pertaining to a homogeneous arch of stone should approximate sufficiently near to the truth to give results of practical importance.

For thick mortar joints of common mortar or for brick arches the theory proposed may be a rude guide, but it is not pretended that it can be anything but a rough approximation to the truth, so that the depth of key for such arches had better be increased empirically over the depths given by the theory above for a homogeneous solid arch.

The theory of the solid arch supposes immovable abutments and it requires three conditions to be fulfilled when the *arch ring* is under stress from its own weight and the weight of backing, roadway, etc., and any loads that may be placed on it in any position:

1. The end tangents, at the springing, to the center line of the arch ring, must remain fixed in direction;
2. The deflection of one end of the arch ring below the other, due to its deformation under stress, must be zero;
3. There must be no change in span due to the deformation of the arch ring.

Analytical theories of the solid arch have been developed by Winkler, Greene and others, and the graphical solution has been given by Prof. H. T. Eddy, to which the writer has contributed his mite.

In *Van Nostrand's Engineering Magazine* for January and November, 1879, the writer claimed that the theory of the solid arch was the most exact solution of the voussoir arch, and a graphical treatment was given in the last named article. In the same year Castigliano, Winkler and Greene referred the treatment of the voussoir arch to that of the solid arch, and finally, in 1893, the writer, in the second edition of "Theory of Voussoir Arches," has given extended applications of the theory of solid arches to voussoir arches by two distinct methods, one founded on the analytical method in part and the other entirely graphical.

These methods were independently applied to a number of stone arch bridges, whose rise was one-fifth the span, for a loading known as Cooper's "Class Extra Heavy A," so placed as to produce the maximum departure of the resistance curve from the center line of the arch ring, and the results appear to be of such importance as to offer some apology for writing this article.

In the stone arch bridges examined the specific gravity of the voussoirs was assumed at 140 pounds per cubic foot, and the density of the spandrel backing was taken at eight-tenths that of the voussoirs. The weight of this backing and any loads on the bridge was assumed to be transmitted vertically to the arch. It is true that this may not be exactly true; in fact, the spandrel may act as an arch itself to some extent, still such additional security may be supposed to neutralize the *dynamic* effect of moving loads, the *static* effect of the loads being met by designing the arch ring, supposed of constant section throughout, so that for the most unfavorable position of the load, for *any* joint, the line of the centers of pressure on the various joints should

be contained within the middle third of the arch ring, and for the joint where the departure was greatest this line should just touch the middle third limit. A slight decrease in the depth of key would thus cause the true resistance curve to pass slightly outside the middle third at some joint or joints.

The proper depth of key to meet this last condition was found tentatively by assuming successive depths of key for the same span until one was found in which the true resistance curve could just be inscribed in the middle third for the most unfavorable position of the live load. Only two trials were needed in any case.

It was found for the arches so designed that no sliding could occur along any joint. The maximum stress, in tons per square foot, at the most compressed edge, varied from nine for the twenty-five foot span to thirty-six for the 150 foot span.

Thus the arch ring possessed the requisite stability for an arch of sandstone or limestone and an excess of stability for granite, whose weight per cubic foot is over the 140 assumed. For material weighing over 140 pounds per cubic foot the depth of key given below can be slightly diminished or a heavier load can be assumed.

The live load assumed is known in Cooper's Specifications as "Class Extra Heavy A."

We give below the distances in feet from the front pilot-wheel to each pair of wheels in turn, and on the same line the weight of the pair of wheels in tons of 2,000 pounds:

Pair of Pilot-wheels.....	0	feet.....	8	tons.
“ Driver-wheels.....	8.1	“ .....	15	“
“ “ .....	13.83	“ .....	15	“
“ “ .....	18.33	“ .....	15	“
“ “ .....	22.83	“ .....	15	“
“ Tender-wheels.....	29.92	“ .....	9	“
“ “ .....	34.75	“ .....	9	“
“ “ .....	40.42	“ .....	9	“
“ “ .....	45.25	“ .....	9	“
“ Pilot-wheels.....	54.25	“ .....	8	“

The second locomotive can be located from the last pair of pilot wheels.

For spans of fifteen feet and under, a pair of wheels carrying forty tons was used as producing a more hurtful effect. The above load was placed over one-half of the arch, roughly speaking, the heaviest part being over the center of the haunch. Its exact position, however, was determined very carefully so as to produce the most hurtful effect upon the arch ring.

An approximation to this load was made by omitting the pilot-wheels in some of the computations. Also by the independent partly analytical treatment, used as a check, the load on drivers was supposed uniformly distributed as well as that on the tenders, and for convenience the lengths of each portion were slightly changed to suit the divisions of the arch required in the theory. The pairs of wheels were supposed to bear on cross-ties eight feet in length, so that only one-eighth of this load was supposed to bear on a slice of the arch contained between vertical planes perpendicular to the axis of the arch and one foot apart.

The depths of key so determined for arches of constant section and rise =  $\frac{1}{5}$  span are given in the following table, the determinations for the spans 12.5, 25, 50, 75, 100, 125 and 150 having been found directly, the others by interpolation from these values. All dimensions are in feet.

RISE EQUAL ONE-FIFTH THE SPAN.

SPAN.	KEY.	SPAN.	KEY.	SPAN.	KEY.
5	1.96	55	3.7	110	5.80
10	2.12	60	3.9	115	5.95
12.5	2.20	65	4.1	120	6.10
15	2.27	70	4.3	125	6.25
20	2.43	75	4.5	130	6.40
25	2.60	80	4.7	135	6.55
30	2.77	85	4.9	140	6.70
35	2.95	90	5.1	145	6.85
40	3.13	95	5.3	150	7.00
45	3.30	100	5.5	155	7.15
50	3.50	105	5.65	160	7.30

Stone arches of the dimensions given should be perfectly safe against rotation or sliding anywhere for the very heavy rolling load assumed; but the depth of key should not be less than the values given, as the true line of resistance, for certain positions of the moving load, will then pass outside the middle third at certain joints, and although the arch may be stable, the factor of safety is reduced too much and the joints of rupture may open, thus admitting the infiltration of water, which is not desirable; besides, for the larger arches, the maximum intensity of stress at the edges of the joints of rupture may exceed safe limits. In fact, this intensity for the 150-foot span for a 7-foot key is 36 tons per square foot—an admissible value for good solid voussoirs, well laid, though not at all for rubble construction or for brick, except, perhaps, the very best pressed brick. From experience it would seem that an outside limit for this intensity for good granite should be about 46 tons per square foot.

The arch can preferably be built by increasing the radial length of joint as we go from the crown to the springing, as is done in arches of large span, in which case the depth of key-stone can be decreased somewhat below the tabular values with the same security against overturning, sliding or crushing.

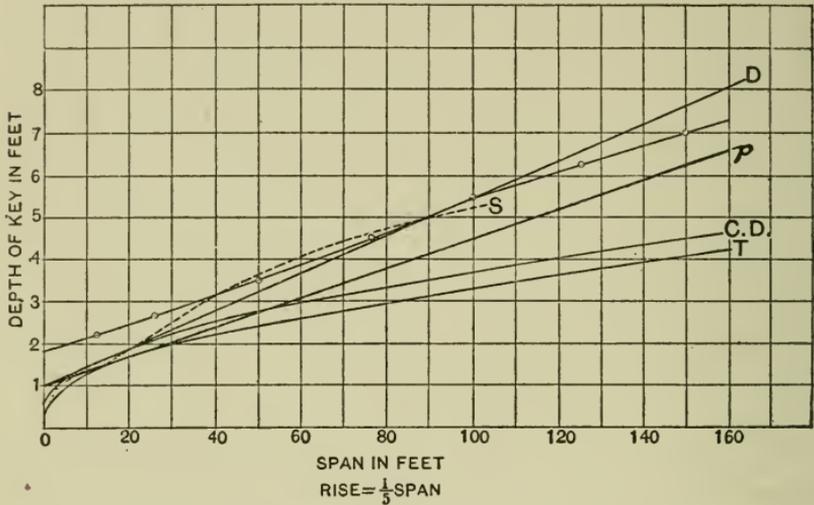
In case the abutments or piers yield somewhat at the top from defective foundations the depth of key should be greater than as given in the tables.

The formulas that have been proposed for depth of key by many authorities are not founded on theory, but on the successful practice of the past, particularly for common road bridges and railroad bridges subjected to the lighter loads of several decades ago.

The writer has been convinced for a number of years that the dimensions given by many of these formulas (in current use to-day) are very inadequate for stone arches subjected to the very much heavier rolling loads of to-day, and that arches so proportioned probably are saved from destruction only from the extra resistance afforded by the span-

drels. On that account he was led to undertake the very serious labor of computing the depths of key for a number of arches after the theory proposed, and to compare with the results given by some of the empirical formulas.

The results are shown graphically in the figure, the line through the small circles (which is nearly straight) being plotted from the values given in the table above.

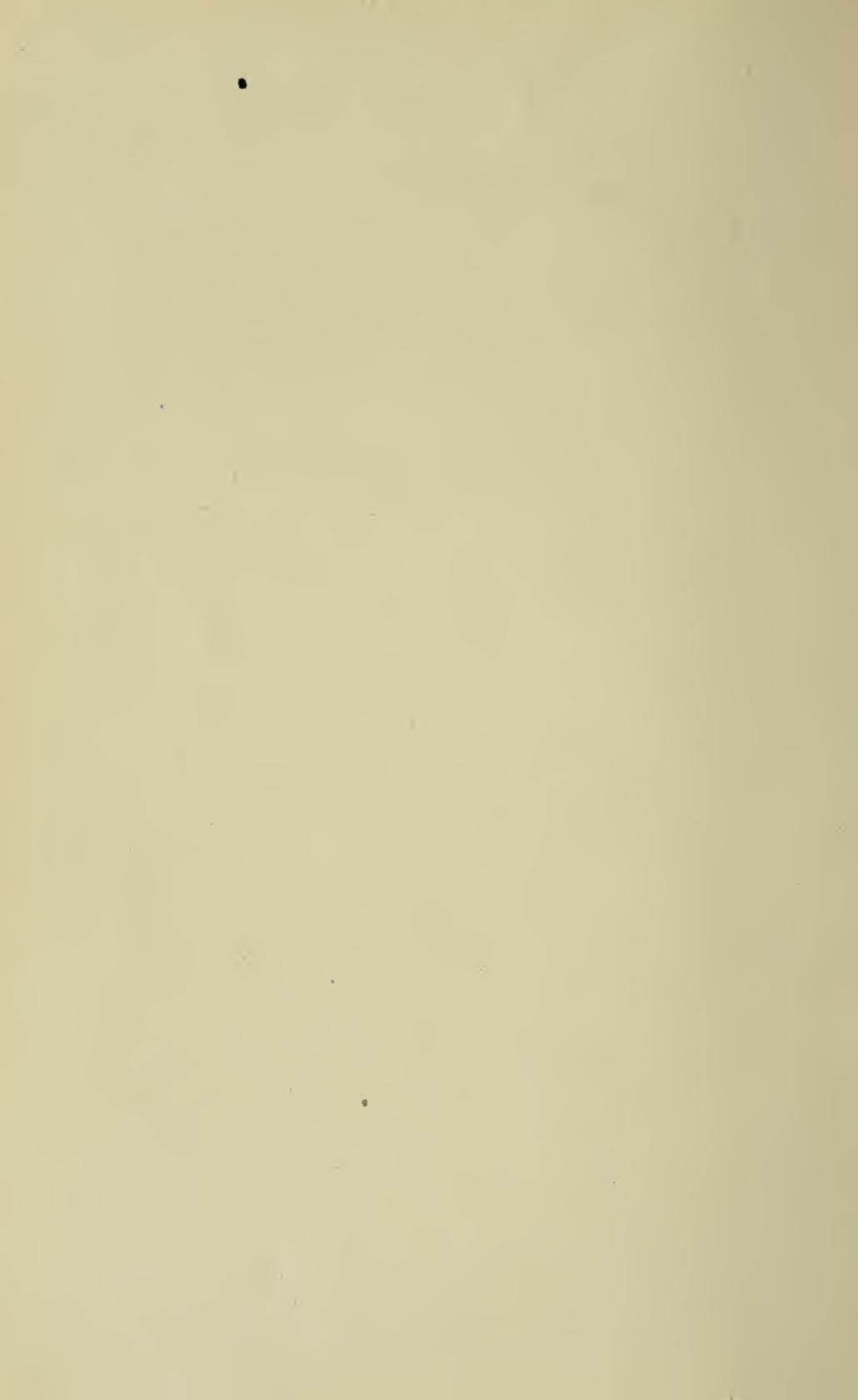


The depths of key proposed by the following authors are given by the ordinates to the various lines for the corresponding spans given by the horizontal lines: Trantwine (line T), Croizette-Desnoyers (line C-D), Perouet (line P), Scheffler, by interpolation from his tables (line S, dotted) and Dejardin (line D).

These results refer to materials of only average strength (second-class masonry for the Trantwine line) and vary very greatly; thus for an arch of 160 feet span and thirty-two feet rise Trantwine gives a depth of key of 4.3 feet, whereas Dejardin requires eight feet and then increases the radial length of joint according to the secant of the inclination of the joint to the vertical as we approach the abutment.

The theoretical depths of key agree more nearly with those of Dejardin and Scheffler than with any of the others, though it is in excess for the smaller spans over any of the empirical results, as should naturally be expected.

It is respectfully submitted to constructors that most of the formulas in current use are inadequate to give a proper depth of key for the very heavy rolling loads of to-day, although it is thought that such formulas may still serve the purpose of a rough guide in the design of common road bridges, unless heavy concentrated loads, as steam road-rollers, are to pass over them. In all cases it is best to use the formulas for an assumed key and then by a theoretical treatment determine the proper key by one or two trials.



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A COMPARISON OF THE METHODS OF SEPARATION AND ESTIMATION OF ZIRCONIUM.

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CHAS. BASKERVILLE.

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The object of the research, whose results are recorded in this paper, was to compare some of the more prominent methods in use for the determination of zirconium. The directions, as found in the literature of the subject, were as closely followed as possible. At times however they were so indefinite that wide limits were given the analyst. In such cases, several experiments were carried out under varying conditions, so that the accuracy of the method might be fully tested.

It was further desirable in this work to examine any suggestion arising, by which a new method of determination might be devised and its accuracy as well tested. Whenever it seemed necessary the purity of the reagents was carefully proved.

Two solutions were used:

- 1st. A solution of zirconium chloride purified by crystallization from hydrochloric acid. This contained free acid.
- 2nd. A solution made by saturating dilute sulphuric acid (4:1) with zirconium hydroxide. This solution was acid to litmus.

The strength of each was determined by evaporating to dryness, igniting the residue and weighing the  $ZrO_2$  obtained. Amounts taken for the experiments were measured from these solutions by means of a calibrated standard burette with a small outlet.

#### THE DETERMINATION OF ZIRCONIUM.

##### *I. Experiments with Ammonium Hydroxide.*

Ammonium hydroxide precipitated the zirconium completely from a cold solution in either a small or large excess. If the solution be hot, however, the excess of ammonium hydroxide must be boiled off, *i. e.*, the precautions taken when aluminium hydroxide is precipitated must be heeded. The precipitate is white and flocculent, settles quickly, is easily filtered and washed with hot water. In most of the experiments carried out this precipitate was washed until the wash water gave no further precipitate, or only a slight cloudiness, with silver nitrate. The precipitate was ignited and heated over the blast lamp until there was no further loss of weight, the residue weighed being taken as pure zirconium dioxide.

The following results were obtained:

<i>Numbers.</i>	<i>Found.</i>	<i>Used</i>
20	0.1082	0.1083
21	0.1624	0.1626
22	0.1081	0.1083
23	0.1618	0.1626
24	0.1098	0.1083
25	0.1647	0.1626
26	0.1090	0.1083
27	0.2812	0.2808
28	0.2832	0.2815

Nos. 20-26 inclusive were made from the chloride solution and Nos. 27-28 with the sulphate. No. 20 was carried out in the cold with a large excess of ammonium hydroxide. The solution was diluted to about 150 c.c. and the precipitate washed with cold water. No. 21 was also cold, the precipitate being obtained by ammonium hydroxide (sp. gr. 0.97) drop at a time. On addition of the fourth drop the precipitation was complete. No. 22 had also only a slight excess of ammonium hydroxide, but the zirconium was precipitated hot. No. 23 shows the necessity for boiling off the excess of ammonium hydroxide. It was precipitated from a hot solution by a large excess of ammonium hydroxide (10 c.c. sp. gr. 0.97). Nos. 24 and 25 respectively contained a slight and large excess of ammonia, but the boiling was continued for fifteen minutes in each case. No. 26 was diluted to about 100 c.c. (the others were diluted to about 150 c.c.) and 20 c.c. of concentrated ammonia water (sp. gr. 0.92) added and that boiled for fifteen minutes. No. 27 was carried out hot, the slight excess of ammonium hydroxide added being boiled until there was only a faint odor of it left. No. 29 was precipitated by adding 50 c.c. concentrated ammonia water (sp. gr. 0.92). The whole solution in this case amounted to about 100 c.c. This was boiled twenty minutes. Most of the ammonia had disappeared.

Since zirconium is frequently precipitated in a chloride solution when the alkaline chlorides are also present, it seemed advisable to note the effect the presence of these substances had on the determination by means of ammonium hydroxide. Experiments were therefore made with the zirconium chloride dissolved in ten per cent. solutions of ammonium, sodium, and potassium

chlorides. These solutions were at first clear, but on boiling 5—15 minutes, at first a slight turbidity was noticed. This increased on boiling until a good precipitate was formed. With potassium chloride this precipitate was curdy and incomplete. Paykull<sup>1</sup> speaks of the formation of double chlorides in the dry way. These precipitates which are very probably similar compounds are now being investigated in this laboratory. It was noted that ammonium chloride did not interfere with the determination, as it was easily volatilized when the crucible was ignited over the blow-pipe. The fixed alkalis however interfered, giving high results. These compounds are of interest.

The following determinations were made in the presence of ammonium chloride :

<i>Numbers.</i>	<i>Found.</i>	<i>Used.</i>
59	0.1106	0.1104
30	0.1070	0.1070
31	0.1077	0.1070

## *II. With Sodium Thiosulphite.*

Sodium thiosulphite, if added as solid crystals to a zirconium chloride solution, previously neutralized with ammonium hydroxide, and then boiled for several minutes, caused complete precipitation. The solid thiosulphite was added up to ten and even twenty per cent. of the solution. The precipitate did not form immediately on addition of the solid thiosulphite, even if the solution was hot, but was rapidly produced after a few moments heating. The precipitate, which settled quickly, was filtered hot and washed with hot water

(1) Ber. VI. 1467.

until the wash water amounted to about twice as much as the original solution. This amount of washing was arbitrarily chosen, as it was found that if it was considerably less the results ran high, showing imperfect washing, due to the presence of sulphite, no doubt. The presence of free acid (one per cent. and less) interfered considerably, preventing complete precipitation (39 and 40-*vid.* below). Moreover the precipitate was finely divided and ran through very close filter paper (S and S, No. 590) along with much free sulphur. The precipitation was made in the cold as well, but in that case, it was found necessary to let the solution remain covered for at least twenty-four hours with occasional stirring. The larger portion of the flocculent precipitate collected well at the bottom of the beaker, but a small portion clung persistently to the stirring rod and sides of the beaker, refusing to come off, even on the most vigorous rubbing with a "policeman."

This reagent will not serve as a precipitant for the zirconium sulphate solution, since the precipitation was found to be incomplete on addition of as much as twenty per cent. of solid sodium thiosulphite to a thoroughly neutralized solution. Preliminary experiments were made with more or less free sulphuric acid present and varying amounts of the thiosulphite (two to twenty per cent.) in solution and solid form, hot and cold.

These determinations were made:

<i>Numbers.</i>	<i>Found.</i>	<i>Used.</i>
33	0.1102	0.1104
34	0.1101	
35	0.1106	
36	0.1645	0.1635
37	0.1079	0.1104
38	0.1641	0.1635

39	0.0645	0.1104
40	0.1538	0.1635
41	0.1107	0.1104
42	0.1093	0.1104
44	0.1080	0.1083
45	0.1215	0.1296

Nos. 41 and 44 were carried out as first recommended above. Nos. 33 and 34 were in the cold, the former with one per cent., and the latter with three per cent. of sodium thiosulphite. No. 36 had also three per cent., but was boiled. No. 37 shows that a very small amount of sodium thiosulphite will throw down most of the zirconium, as only five drops of a ten per cent. solution were added in the experiment. The precipitation was complete on addition of the thiosulphite up to two per cent. (No. 38,) but the precipitate crept and only a portion settled well. Nos. 39, 40 and 42 show the varying interference of free hydrochloric acid, and No. 45 was a neutralized sulphate solution with twenty per cent. of solid sodium thiosulphite.

### *III. With Potassium Sulphate.*

The very old method for separation, which Berzelius<sup>3</sup> used for want of a better, and one recommended for use in a great number of text books now, is the precipitation of a zirconium sulphate solution as a basic zirconium potassium sulphate, which according to Paykull<sup>4</sup> may have the formula,  $K_2SO_4 \cdot 2[ZrO_2 \cdot Zr(SO_4)_2] + 14H_2O$ . This would be best brought about by adding an excess of a saturated potassium sulphate solution to a neutralized concentrated solution of zirconium sulphate. The pre-

3. Pogg. Ann. III-208.

4. Ber. VI-1467, and XII-1719.

precipitation however was incomplete even in neutral solutions. The text books vary in regard to the properties of this double sulphate; some<sup>5</sup> state the precipitate to be insoluble or sparingly soluble in either water or hydrochloric acid; another<sup>6</sup> states its solubility in water alone and points out the danger of loss in the necessary washing. Rose<sup>7</sup> referring to Berzelius<sup>8</sup> avoids this loss by washing with dilute ammonium or potassium hydroxide. These contradictory properties were all noted in Watt's Dictionary.

An experiment was carried out to learn the actual deportment of this salt in the presence of water. A fairly concentrated solution of zirconium sulphate, containing ten per cent. of  $ZrO_2$ , was completely neutralized with ammonium hydroxide until a permanent precipitate was formed and this dissolved in two or three drops of dilute sulphuric acid. This was done with a boiling solution. To this was added an excess of a saturated potassium sulphate solution. The beaker was placed in cool water. When cold the supernatant liquid, the flocculent precipitate having settled well, was decanted through a tared filter. This filtrate, was tested with more potassium sulphate, boiled and cooled, but no further precipitation occurred. On addition however of some ammonium hydroxide a white precipitate was thrown out, showing either that the potassium sulphate did not precipitate the zirconium completely or the precipitate was soluble in water. The precipitate was washed several times by decantation and the filtrate in each case showed the solubility of the salt.

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5. Roscoe and Schorl. vol. II, part II-p. 271., and Regnault *Chimie* II-285, and Wöhler *Handbüch Anorg. Anal.* p. 117.

6. Pelouse et Fremy *Traité de Chimie Générale* III-523 2nd Ed.

7. *Analyt. Chem.* translated by Griffin.

8. Poggendorff's *Annalen*, IV.-136.

There remained to learn the completeness of the precipitation, Another experiment similar to the above was carried out bearing in mind the suggestion of washing with a solution of ammonium hydroxide, at first with potassium sulphate to be sure that there was an excess of that reagent present and then with ammonium hydroxide. The precipitation had not been complete. After several washings, when the original solution might well be presumed to be removed, or the major portion at least, the wash water (very dilute ammonia water) gave no evidence of the presence of zirconium. Several experiments were carried out, but in only one case was the double salt weighed. It gave about ninety per cent. of the zirconium really present. The filtrates from several were examined and it was learned that from one to ten per cent. was always lost, the amount depending on the exact conditions of precipitation and the amount of washing succeeding. The objection to using ammonium hydroxide as wash water when it was desirable to separate zirconium from iron, aluminium or titanium, is easily seen.

The conclusion arrived at was, that the precipitation of zirconium as a double sulphate with potassium afforded no quantitative means of determination for that metal, nor of separation from aluminium, iron or titanium.

#### *IV. By Sodium Carbonate.*

Sodium carbonate precipitated solutions of zirconium salts completely. A great difficulty arose, however, in the exceeding slowness of filtration and practical impossibility of washing the precipitate free from the alkaline carbonate. A single result, obtained from several analyses, was

	<i>Found.</i>	<i>Used.</i>
ZrO <sub>2</sub>	0.1785	0.1723

#### V. *By Ammonium Carbonate.*

When a saturated solution of ammonium carbonate was added gradually to a zirconium chloride solution, at first a white flocculent precipitate was thrown down. This seemed to be produced by the free ammonia present, but on a further addition the solution became clear again. If this was boiled, a clear flocculent precipitate came down. The boiling was continued for about fifteen minutes, when the carbon dioxide had ceased to come off. The appearance of this precipitate was exactly that produced by ammonium hydroxide, yet the filtration was very slow, as in the case with the other alkaline carbonate. In some hundred and more precipitations by means of ammonium hydroxide, I have never failed to secure the zirconium hydroxide in such a condition as to filter rapidly. This was very likely a basic carbonate, which required continued heat with the blow pipe for constant weight. Such a precipitate when ignited gave 0.1733 g. ZrO<sub>2</sub> when 0.1723 g. was used.

#### VI. *By Ammonium Oxalate.*

L. Svanberg,<sup>9</sup> because oxalic acid failed to give a complete precipitation of zirconium, thought the solution contained a new element, which he called *norium*. Sjögren<sup>10</sup> in his analyses of the mineral catapleiite said; "Eine nicht saure Lösung der Erde aus dem Katapleiite

9. Ofversigt of R. V. Akad. Förhandl. 1845, p. 37.

10. Pogg Ann. 1852, Ergänzung, III. p. 469. J. Prakt. Ch. 55, 298.

wird wohl von oxalsaurem Ammoniak gefällt, aber dieser Niederschlag löst sich nicht nur in einem Ueberschusse des Fällungsmittels, sondern auch in einem geringen Zusatz von Oxalsäure." Berlin,<sup>11</sup> however, also said: "\* \* \* dass der durch dieser Salz (ammonium oxalate) in einer Lösung von Zirkonerde bewirkte Niederschlag bei einem Ueberschusse des Fällungsmittels wieder verschwindet. \* \* \* Aus dieser Auflösung schlägt Ammoniak die Zirkonerde vollständig nieder." Hermann<sup>12</sup> repeated all previous experiments, and not only corroborated Berlin's observations, but determined the best conditions for this precipitation. He noted that in an excess of the precipitant (ammonium oxalate), only four-tenths of all the zirconium was precipitated. Such has been the result of my own experiments, save the determination of the rate of precipitation as done by Hermann.

#### *VII. By Potassium Hydrogen Oxalate.*

Behrens(13) in his "Contributions to Micro-Chemical Analysis" notes that zirconium can be detected with extreme delicacy (0.0005 m.gr.) by that means. For quantitative purposes, however, potassium hydrogen oxalate could not be used, as the precipitate formed was soluble in an excess of the precipitant, but an incomplete precipitation took place on boiling.

#### *VII. By Hydrogen Peroxide.*

(See Separation Zirconium and Titanium.)

#### *IX. By Sulphur Dioxide.*

Because of the analogy of the elements, I was led to

11. J. Prak. Ch. 58—145.

12. J. Prak. Ch. 96—332.

(13) Zeit. Anal. Chem. translated in Ch. News, XLIV—124.

try a method commonly used with titanium, viz.: prolonged boiling of a potassium hydrogen sulphate fusion in dilute solution with sulphur dioxide in excess. On application of this method, however, on the prepared sulphate (see above), I failed even after boiling four hours with an excess of sulphur dioxide, to obtain a precipitate, if the solution was acid. If the solution was nearly neutralized with ammonium hydroxide, and then boiled with an excess of sulphur dioxide, after being greatly diluted a precipitate was produced. This precipitation, however, was incomplete, even after boiling six hours or passing steam through the same for two or three hours. The precipitate too was very finely divided, running through the closest filter papers at my command. Therefore this method could not be used.

But on addition of sulphur dioxide to the chloride solution, even in the cold, and if it was acid, a dense white precipitate was immediately noted. On boiling with an excess of sulphur dioxide in a neutralized solution, *i. e.*, the chloride solution, neutralized by ammonium hydroxide until the slight precipitate was no longer dissolved by boiling, and this precipitate then taken up with two or three drops of dilute hydrochloric acid, the separation of the zirconium was complete.

The accuracy of this method is shown by the following results:—

<i>Number.</i>	<i>Found.</i>	<i>Used.</i>
81	0.1074 )	0.1077
81	0.1078 (	
82	0.1043	0.1038
83	0.1070	0.1077
84	0.1047	0.1050

The precipitation took place immediately on addition of sulphur dioxide and after two minutes boiling the precipitate settled quickly and was easily filtered.

This method then is applicable to the chloride only and a sulphate would have to be first changed to chloride by precipitation with ammonium hydroxide and resolution in hydrochloric acid. This was done and 0.2815 g.  $ZrO_2$  was found when 0.2812 g. was used.

The presence of large amounts of such salts as ammonium chloride did not aid the precipitation of the sulphate. The presence of free hydrochloric acid must be avoided and it is best to use a fresh solution of sulphur dioxide or the gas direct.

#### SEPARATION OF ZIRCONIUM FROM IRON.

##### *I. By Ammonium Sulphide in an Ammoniacal Tartrate Solution of their Salts.*

Rose<sup>14</sup> knew the property tartaric acid possesses of rendering solutions of a number of metallic oxides incapable of precipitation by alkalis. However he made use of just such a solution, by adding to it an excess of ammonium sulphide, to separate iron from zirconium. He said, "If to the solution of these two bases a *sufficient* quantity of tartaric acid has been added, the addition of an excess of ammonia produces no precipitate. "I found five times as much tartaric acid as iron present was a "sufficient quantity," but an excess, five per cent. of the whole solution, had no ill effect, although such a large excess is not necessary. If the iron was present in the same amount as the zirconium, the separation was found to be incomplete, if only one precipitation of

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14. *Analyt. Chem.* translated by Griffin, p. 58.

the iron was made. The zirconium dioxide could not be obtained perfectly white, but possessed from a yellow to a brown color due to the iron present. However, if the amount of iron be small, five per cent. and less, as it occurs in the mineral zircon, the separation was thorough and the ignited zirconium dioxide obtained was snow white and iron free.

Two analyses are given :—

	<i>Found.</i>	<i>Used.</i>
ZrO <sub>2</sub> —	0.1119	0,1118
	0.2815	0.2818

The process was as follows: To the solution of the salts, tartaric acid, best solid, to five times the amount of iron present, was added, and this neutralized by an excess of ammonium hydroxide, and then ammonium sulphide in excess. This was warmed slightly, covered, and set aside to settle. The supernatant liquid must acquire a yellow color before filtration. To avoid this delay, one experiment was carried out by boiling and direct filtration. Time was thereby saved. The precipitated iron sulphide was washed quickly with a dilute ammonium sulphide solution. The filtrate was evaporated in a porcelain dish on a water bath until it became of small bulk, when it was transferred to the crucible, in which the final residue was to be weighed. Sometimes it was noticed that there was a further separation of iron sulphide during this evaporation. This was filtered off before the concentration became too great without causing any error in the final result. The crucible when apparently dry was heated for several hours in an air bath at 100 °C. and then ignited, top on. After the volatile portion of this residue was driven off, the lid was removed and all the carbon burned away.

The crucible was then heated with the blow pipe until the weight was constant. This required at least an hour if a porcelain crucible was used.

The method was carried out by the writer as given above and accurate results, as noted, obtained, when the iron was no more than five per cent of the two metals present. The iron was not determined. The great amount of time required was the only objection to be noted.

*II. By Ammonium Hydroxide, Ammonium Sulphide and Sulphurous Acid.*

Berthier<sup>15</sup> said that if a mixture of the salts of iron and zirconium in solution be precipitated by an excess of ammonium hydroxide and then an excess of ammonium sulphide be added, that the ferrous sulphide formed could be dissolved out with a sulphurous acid solution. Several experiments were carried out. The solution was precipitated by an excess of ammonium hydroxide,—in one the excess was boiled away—then an excess of freshly made ammonium sulphide was added and the whole allowed to settle. (Experiments were made with both the colorless and yellow ammonium sulphide). The supernatant liquid was drawn off, or the whole filtered, and the precipitate boiled with a strong sulphurous acid solution. Most of the black sulphide became immediately decolorized. After a five or ten minutes boiling, the solution was filtered and washed with hot water and a weak sulphur dioxide solution. The precipitate remained brown however, strongly colored by the iron which had not been dissolved. In one experiment this impure precipitate was redissolved

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15. Booth's *Encycl. Chem.*

in dilute hydrochloric acid and the process repeated. There was only a slight diminution in the amount of iron left. If the hydrochloric acid solution of this precipitate was neutralized by ammonium hydroxide and then an excess of sulphurous acid added, the zirconium separated out perfectly white and free from iron,

<i>Found.</i>	<i>Used.</i>
ZrO <sub>2</sub> —0.1070	0.1070

The method of Berthier as I carried it out did not give satisfactory results.

### *III. By Sodium Thiosulphite.*

With proper precautions zirconium was completely separated from iron by means of sodium thiosulphite. The directions given for this method were not always specific.<sup>16</sup> It was noted (by the writer) that unless the solution be neutralized, the precipitation would be incomplete; also if it be neutral and the boiling long continued, the precipitate might be very finely divided and hard to catch on the filter paper; also if all or the greater part of the sulphur dioxide be boiled away the oxide of iron separated immediately on access of the air after the removal of the clock glass used to cover the beaker. No accurate separation was obtained if the solution was rendered neutral with ammonium hydroxide or the precipitation was made when the solution was hot.

But the method of Chancel<sup>17</sup> and Stromeyer<sup>18</sup> gave accurate results. By this method the solution was rendered neutral with sodium carbonate, the beaker

16. Rosc. and Schorl. II—sI—271., and Miller's Chem. II—p. 643.

17. Ann. Ch. Pharm. CVIII 237.

18. *Ibid*, CXIII-127.

placed in cold water, and when the solution was cooled, an excess of sodium thiosulphite was added. After the solution became decolorized, it was boiled, and the white precipitate (zirconium hydroxide according to Stromeyer) settled out well. This precipitate was easily filtered, washed with hot water, burned and ignited to constant weight.

These results are reported :—

<i>Numbers.</i>	<i>Found.</i>	<i>Used.</i>
140	0.1315	0.1333
141	0.0552	0.0565
143	0.1640 )	0.1614
145	0.1613 (	

Nos. 140 and 141 were in solutions in which there was present free acid—No. 140 hydrochloric—and No. 141 sulphuric. No. 143 was not properly neutralized and on addition of the sodium thiosulphite, a heavy flocculent flesh-colored precipitate settled out. This on warming became white, but when the precipitate was burned showed the presence of some iron. No. 145 was carried out exactly according to the directions given above.

#### *IV. By Ammonium Sulphite.*

As I carried out the experiments, I failed to succeed in perfectly separating iron and zirconium by this method, which is also recommended by Berthier.<sup>19</sup> Solutions of the chlorides of these two metals were made with equal and varying amounts of each, then an excess of freshly prepared ammonium sulphite was added. The zirconium sulphite precipitated was soluble in an

<sup>19</sup> Booth's *Encycl. Chem.* 1850.

excess of the precipitant, but zirconium hydroxide was thrown down on boiling. If the boiling was kept up until no more sulphur dioxide came off, immediately on permitting the liquid to come into contact with the air, a scum of oxide of iron formed. Next, the boiling was not continued so long—the precipitate when burned, however, still contained some iron. Besides the results obtained were low, as may be seen by these analyses:—

<i>Number.</i>	<i>Found.</i>	<i>Used.</i>
150	0.0463	0.0535
152	0.0871	0.1070
156	0.0453	0.0535

The hydroxide is, doubtless, partly soluble in an excess of the sulphite, even after boiling.

#### V. *By Sulphur Dioxide.*

The method of precipitation of zirconium from a chloride solution on addition of sulphurous acid in excess affords an excellent means of separating zirconium from iron. The zirconia precipitated by sulphur dioxide in large excess and boiled two to three minutes, was, after filtration, washed four or five times with hot water. The further necessary precautions have been given above. The iron was titrated in the filtrate.

The experiments gave these results.

<i>Number.</i>		<i>Found.</i>	<i>Used.</i>
160	} ZrO <sub>2</sub>	0.1047	0.1043
	} Fe	0.0830	0.08225
161	} ZrO <sub>2</sub>	0.1074	0.1070
	} Fe	0.08248	0.08225
162	} ZrO <sub>2</sub>	0.1078	0.1070
	} Fe	0.0820	0.08225

163	{	ZrO <sub>2</sub>	0.1043	0.1043
	{	Fe	0.04389	0.04225
166	{	ZrO <sub>2</sub>	0.0537	0.0535
	{	Fe	0.04334	0.04225

## SEPARATION OF ZIRCONIUM FROM ALUMINIUM.

*I. By Sodium Hydrogen Carbonate.*

Having noted the property of zirconium of being reprecipitated from a solution (at first precipitated but soluble in an excess of sodium hydrogen carbonate) on boiling with ammonium chloride, Pelouse and Frémy<sup>20</sup> proposed it as a method of separation of that metal from aluminium. Several experiments were carried out by the author of this paper, but the conclusion arrived at was that it was a qualitative separation, which could not be used for quantitative purposes.

*II. By Sodium Iodate.*

Davis<sup>21</sup> gives a neat and accurate method for the separation of zirconium and aluminium. The directions, as given by him, for the process must be most carefully followed in order to obtain accurate results. Moreover the process is inapplicable when iron, be it in a ferrous or ferric condition, is present. The method therefore offers but little of practical value in ordinary analysis.

“Their<sup>22</sup> (aluminium and zirconium) solution in hydrochloric acid is treated with sodium carbonate until a permanent precipitate is formed. This precipitate is

20. *Traité de Chimie Générale*, III-523, 1854 Edition.

21. *Am. Ch. J.*, XI-26.

22. *Ibid.* p. 29.

dissolved in the smallest possible quantity of dilute hydrochloric acid and sodium iodate ( $\text{NaIO}_3$ ) added in excess. The solution is heated for about fifteen minutes. It is then allowed to stand twelve hours filtered, washed down with boiling water, dissolved in hydrochloric acid and finally precipitated with ammonia, ignited and weighed." I found in an analysis 0.0515 g.  $\text{ZrO}_2$  when I had used 0.0520 g.

Analyses were made also according to his recommendation of the use of from five to ten per cent. of sodium chloride. The results obtained were high, doubtless due to imperfect washing. An example :

	<i>Found.</i>	<i>Used.</i>
$\text{ZrO}_2$	0.0596	0.0520

The numerous experiments made served merely to confirm Davis' work. It was necessary to avoid a too far neutralization with sodium carbonate as the separated zirconium was contaminated with varying amounts of aluminium. The permanent precipitate formed by the sodium carbonate was difficult at times to redissolve in a small amount of dilute hydrochloric acid. Yet an excess of acid must be avoided, for it was learned by experiments, as Davis had noted, that the presence of even 0.1 per cent. by weight of hydrochloric acid would cause low results. Four hours was a sufficient time for complete separation however. An experiment with the sulphate solution showed no action whatever. Even the small amount of sulphuric acid in an aluminium sulphate solution was found to interfere, hence the necessity of having a hydrochloric acid solution, free from sulphuric acid, was apparent. Davis evidently noted this as he was particular in having a pure solution of aluminium chloride in his experiments.

*III. By Sulphur Dioxide.*

Sulphurous acid may be used for the separation of zirconium and aluminium as well. The process is essentially the same as for the separation of iron and zirconium (see above).

The analyses proving this are also given.

<i>Number.</i>		<i>Found.</i>	<i>Used.</i>
201	} $\text{ZrO}_2$ } $\text{Al}_2\text{O}$	0.1042	0.1043
		0.0608	0.0610
207	} $\text{ZrO}$ } $\text{Al}_2\text{O}$	0.1070	0.1070
		0.0316	0.0305

## SEPARATION OF ZIRCONIUM AND TITANIUM.

As is well known, titanium and zirconium are metals possessing many properties in common. Their deportment with reagents is very similar, varying only in degree, as a rule. This fact, and that of the properties of each being further altered by the presence of the other in the same solution,<sup>23</sup> renders their separation extremely difficult. An example of this alteration of properties was noted on boiling a solution of sulphates of these metals. On long continued boiling titanium sulphate, when in solution alone, is completely precipitated. Zirconium sulphate, under the same conditions, produces no precipitate, whereas a mixture of these permits of only a partial precipitation of the titanium, the larger portion remaining undissolved (Berzelius<sup>24</sup>).

*I. By Potassium Sulphate.*

It was not found possible to use the precipitation of

<sup>23</sup> Rose Analyt. Chem, p. 172.

<sup>24</sup> Pogg. Ann. VI., 232.

the zirconium as the basic potassium sulphate, for the reasons above noted. For want of a better method, however, this was for a long time used.

## *II. By Boiling an Acetic Acid Solution.*

Franz and Streit claimed complete separation if the solution, neutralized by ammonium hydroxide, were rendered strongly acid with acetic acid and boiled sometime. The usual preliminary qualitative experiments were carried out by the writer, and he obtained a precipitate in both cases. The titanium was precipitated directly and in large amounts, whilst the zirconium was also precipitated, but in small amounts. Of course solutions of approximately known strength were used in these experiments. When this was noted the completeness of the titanium precipitation was not tested. This method, therefore could not be recommended.

## *III. By Ammonium Oxalate and Ammonium Carbonate.*

The experiments of Hermann<sup>25</sup> were very carefully repeated. The zirconium chloride solution was diluted to contain one part in one hundred parts of water, and to this was added double the weight (of zirconium) of ammonium oxalate. I did observe, as he says,<sup>26</sup> "Dabei entstand anfänglich eine Trübung, nachdem aber die ganze Quantität des Oxalats zugesetzt worden war, klärte sich die Flüssigkeit wieder vollständig auf. Man

25. J. Prak. Ch. 97—338.

26. *Ibid*, 337:

gass jetzt diese Lösung von oxalsaurem Ammoniak-Zirkonerde in eine concentrirte Lösung von kohlensaurem Ammoniumoxyd." But I did *not* observe, "Dabei blieb die Flüssigkeit ganz klar und setzte auch nach längerem Stehen keine Spur eines Niederschlags ab."

A chloride solution of titanium, treated in the same manner as above, gave a heavy precipitate, when the double oxalate formed an addition of the ammonium oxalate, was poured into a saturated solution of ammonium carbonate. As noted above a precipitate was obtained with the zirconium chloride solution as well; nevertheless an analysis was made and 0.0327 g. titanium was found when 0.0302 g. had been used. This proved to the writer that advantage could not be taken of this for a *complete* separation of zirconium from titanium. Hermann<sup>27</sup> noted this incompleteness in his further remarks concerning an experiment he performed: "Die geringe Differenz von 0.18 Theilen Zirkonerde zu wenig und 0.18 Theilen (used 6, found 6.18) Titansäure zu viel kam daher, dass die Titansäure beim Fällen durch kohlensaures Ammoniumoxyd ein geringe Menge Zirkonerde mit niedergerissen hatte."

#### IV. *By Hydrogen Peroxide.*

So no good and accurate method was known until Bailey<sup>28</sup> noted the effect of adding hydrogen dioxide to a zirconium solution. This is the only thoroughly accurate method yet proposed. Its neatness and rapidity in application are to be especially noted. At the same time consideration must be given to the difficulty in obtaining perfectly pure hydrogen dioxide.

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27. *Ibid*, 439.

28. J. London Ch. Soc. Trans. 1886, p. 149.

He proceeded<sup>29</sup> by adding an excess of hydrogen dioxide to a moderately acid solution of a mixture of iron, zirconium and titanium. After twenty-four hours standing in a stoppered flask, the precipitated oxide ( $Zr_2O_3$ ) was caught and filtered, washed and ignited. In carrying out this method the writer noted the necessity of having an acid, yet not too acid, solution. If the solution was first neutralized with ammonium hydroxide or sodium carbonate, the precipitated zirconium oxide was highly contaminated with iron, which could not be washed out.

Analyses gave these results:

<i>Numbers.</i>	<i>Found,</i>	<i>Used</i>
{ $ZrO_2$	0.1111	0.1118
{ Fe	0.0135	0.0138
{ $TiO$	0.0302	0.0302
$ZrO_2$	0.2425	0.2424

The precipitation was found to be complete on boiling the solution two or three minutes to avoid the twenty-four hours delay by standing cold. After filtering from the zirconium oxide, the filtrate was rendered alkaline with ammonia water, filtered and the precipitate dissolved in dilute hydrochloric acid. The excess of acid was neutralized and the titanium determined by precipitation on boiling with sulphur dioxide.<sup>20</sup> The iron was determined from the filtrate from this.

The hydrogen dioxide obtained from the manufacturer<sup>31</sup> was found to contain a large amount of silicic acid in solution along with the other ordinary impuri-

29. *Ibid* p. 482.

30. The author *J. Am. Ch. S.*

31. Dr. Merchand, 28 Prince st., New York.

ties. The strength of this solution was 72 volumes, being brought to this strength according to Thénard's method<sup>32</sup> (Marchand). I further purified and concentrated this to 111 volumes by distilling in partial vacuum, according to Talbot and Moody.<sup>33</sup> I found the potassium sulphate present interfered very much with the reaction by the formation of the more or less soluble basic zirconium potassium sulphate. So nothing definite could be learned from my experiments, which were many, with either the 111 or 72 volume hydrogen peroxide.

To avoid the formation of the compound with potassium sulphate, hydrochloric acid<sup>34</sup> was used. By this method was obtained a solution of the dioxide practically free from silicic and sulphuric acids, but one weaker, being only 55 volumes. It was with this solution the analyses above reported were made.

This method of using hydrogen dioxide is the only accurate method given for the separation of zirconium and titanium. It is direct and rapid, delicate and elegant, but expensive and by no means always convenient.

I cannot close this summation without expressing my great indebtedness to Dr. F. P. Venable, for his ever ready sympathy with and kindness to me in this work. I wish also to express my thanks to Dr. Chas. Marchand, 28 Prince st., New York, for six pounds of 72 volume hydrogen peroxide, with which he kindly presented me.

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33. Mass. Inst. Technology Quarterly, V-123.

34. *Ibid*, 131.

32. *Annales de Chimie de Physique*, [2] 10-114, 335, 11-85.

## PRIMITIVE STREAK AND BLASTOPORE OF THE BIRD EMBRYO.

BY H. V. WILSON.

Embryologists, with but few exceptions, recognize in the bird embryo a gastrula stage. There is, however, a very considerable diversity of opinion as to just what constitutes the gastrula. Leaving aside certain interpretations for which at present there seems no good ground, we find there are two very different views held regarding the nature of this embryonic stage.

According to the older view, advanced by Balfour and Rauber, the essential difference between the bird gastrula and the fish gastrula is that a part of the original edge of the blastoderm, is in the bird turned in to form the primitive streak. Thus while in the fish the blastopore is represented by the blastoderm edge, in the bird it is represented by the primitive streak plus the blastoderm edge. This theoretical view receives the support of the well known researches of Duval on the germ layers of birds<sup>1</sup>. Duval finds that the very young blastoderm of the bird is similar to that of fishes. In both, the ectoderm and entoderm are continuous round the edge, which therefore corresponds to the blastopore. But this precise similarity is only transient, for in the bird the primitive streak soon makes its appearance. The manner in which the primitive streak is formed proves conclusively that it is only a modified part of the blastoderm edge. The young blastoderm (fish-like stage) grows centrifugally at all

1. De la formation du blastoderme dans l'oeuf d'oiseau. *Annales des Sciences Nat. Zoologie.* T. XVIII.. 1884.

points except at that which corresponds to the future tail end of the embryo. By this means a certain portion of the blastoderm edge becomes turned in on each side of the median line in the posterior region, the two portions running forwards side by side to the point already mentioned, where no centrifugal growth occurs. These two portions fuse and form the primitive streak, which thus at first extends to the very edge of the blastoderm. Now, however, centrifugal growth begins at the posterior pole of the blastoderm, and the primitive streak gradually takes up its well known position at a distance from the edge.

In opposition to this view Oscar Hertwig, Rabl, and others claim that the blastoderm edge is not a part of the gastrula mouth, but is a peculiarity of certain mesoblastic ova, and that the blastopore is represented exclusively by a structure known as the *sickle* plus the primitive streak. This doctrine is based on the belief that an ingrowth or invagination of cells takes place only in the region of the sickle and streak, and not round the edge of the blastoderm. In a paper on the development of teleost fish I have already attempted a criticism of this view<sup>2</sup>, and will only add that it is to my own mind in direct contradiction with the admirable account given by Duval of the formation of the primitive streak. On the other hand it receives support from the discoveries of Kupffer on the reptilian embryo, and from Koller's description of the way the streak is formed in the bird embryo.

According to Koller's account<sup>3</sup>, which is adopted by

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2. The Embryology of the Sea Bass. Bulletin U. S. Fish Commission. Washington. 1891, pp. 268-271.

3. Beiträge zur Kenntniss des Hühnerkeims in Beginne der Bebrütung, SB. der König. Akad. d. Wiss. Wien. 1879.—Untersuchungen über die Blätterbildung in Hühnererei. Archiv für Mikros, Anat. Bd. XX. 1881.

Hertwig in his text book, there very early develops a sickle-shaped thickening which lies between the area pellucida and the area opaca, in the posterior region of the blastoderm. A groove, the sickle groove, is present in this thickening, and in the median line there is a short anterior projection called the *sichel-knopf*. The primitive streak is produced by the continuous growth in the median line, of the *sichel-knopf*, and is therefore an outgrowth of the sickle. Since neither the sickle nor the primitive streak is at any time connected with the blastoderm edge, the latter structure cannot be regarded as a part of the blastopore, which is represented exclusively by the two former structures.

The contradiction between Duval's and Koller's account concerns a fundamental feature of the process of gastrulation, and more facts on the early history of the bird blastoderm are much to be desired. Duval himself, in his criticism of Koller's papers (l. c.), states it as his opinion that the sickle is an inconstant feature, of no morphological importance, belonging in the same category as other local thickenings of the blastoderm. I may mention that I have myself looked through very young blastoderms, in which the primitive streak was from one-half to two-thirds the length of the area pellucida, without discovering in the majority of them any trace of the sickle. I am aware that Koller describes the sickle as becoming much less conspicuous with the continued growth of the streak, but his figures of blastoderms<sup>4</sup> corresponding in age to mine, show an evident remnant of the sickle, while I can find no trace of such a structure in the majority of my embryos.

Koller, it will be remembered, kept his eggs at a

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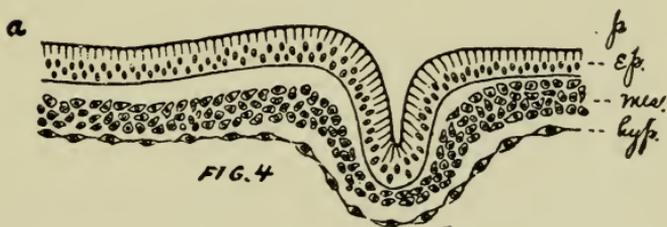
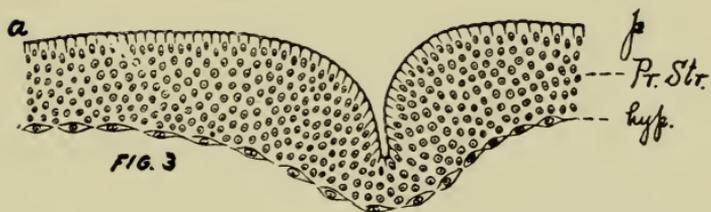
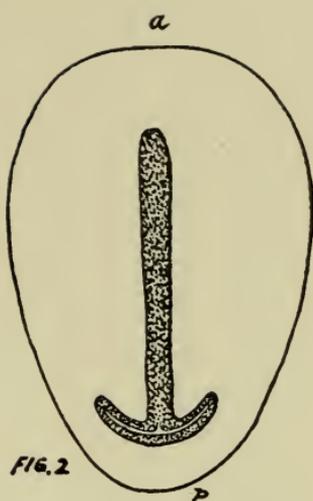
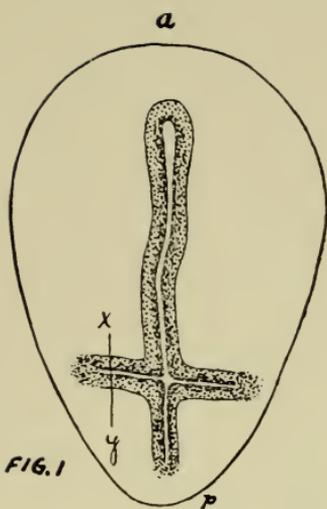
4. SB. d. König. Akad. d. Wiss. 1879, Beiträg. &c., figs. IV.a. IV.b. V.

temperature below the normal temperature of incubation, in order to lessen the rapidity of development. A certain percentage of abnormalities was to have been expected from the use of the temperature below the normal, and I have satisfied myself that at 35° various kinds of abnormalities do occur. Out of a considerable number of young blastoderms, incubated at 35°, while the majority showed no trace of the sickle, in a few cases the primitive streak exhibited abnormalities suggesting more or less strongly the sickle. Surface views of two of these blastoderms are given in Figs. 1 and 2. In the primitive streak of Fig. 2, I could not make out the primitive groove, but the groove was very evident in the sickle at the posterior end of the streak. (Kupffer and Benecke<sup>5</sup> give a wood-cut figure of a chick blastoderm, quite like my figure 2, except that the primitive groove is shown. While they incline to the belief that the sickle in such a blastoderm is of morphological importance, they admit that it was only rarely that such blastoderms were found.) In the blastoderm shown in Fig. 1, the groove was conspicuous, both in the streak and in the transverse outgrowths of the streak. This blastoderm was sectioned longitudinally. A median section through the streak is shown in Fig. 3. The transverse groove is deep; the hypoblast is differentiated as a distinct layer; the epiblast and mesoblast are indistinguishably fused. In Fig. 4 is represented a section lying in the plane  $x-y$  of Fig 1. In this region the transverse groove is as deep as in the median section, but the three layers are separate.

My failure to find the sickle in blastoderms where, according to Koller it should be present, and the obser-

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5. Die ersten Entwicklungsvorgänge am Ei der Reptilien. Königsberg. 1878. p. 11.





vation of abnormalities resembling in a measure the sickle, incline me to accept Duval's view of this structure, and with him to regard it as an inconstant feature of no morphological importance.

Hertwig, in his paper on "*Urmundrand Spina bifida*," (1892), touches on the question of meroblastic gastrulation, and it would seem that he no longer believes in the existence of Koller's sickle. For in his brief sketch of the manner in which the primitive streak is formed, he follows Duval, and represents the streak as arising by the coalescence the blastoderm edges. He therefore comes to regard the edge of the young blastoderm as the blastopore.

Hertwig does not look on the entire edge of the young blastoderm as the blastopore, but for some reason unknown to me divides it into a blastoporic part and a part designated as the *Umwachsungsrand*, by which name he formerly (text-book) meant the entire blastoderm edge. The edge of the teleost blastoderm is likewise divided into blastopore and *umwachsungsrand*. This division is surprising, for round the entire edge of the teleost blastoderm there is an ingrowth of cells, just as there is round the blastopore lip of the amphibian embryo. And the existense of such an ingrowth is undoubtedly a very strong argument for regarding the whole edge as the blastopore. It would be interesting to learn the facts that have induced Professor Hertwig to divide the edge of the teleost blastoderm in this manner.

But if Hertwig has come to regard the edge of the blastoderm, or any part of it, as representing the *urmundrand* in the bird embryo, it would seem that he must have abandoned his former views on gastrulation

in the Sauropsida, and have taken a long step towards the position of Balfour and Rouber.

CHAPEL HILL, NORTH CAROLINA.

Explanation of the figures illustrating Mr. Wilson's paper on "Primitive Streak and Blastopore of the Bird Embryo":

Fig. 1. Surface view of abnormal chick blastoderm. + 16.

Fig. 2. " " + 16.

Fig. 3. Median longitudinal section through the primitive streak of Fig. 1.  $\times 90$ .

Fig. 4. Longitudinal section through line x-y of Fig. 1.  $\times 90$ .

a.—anterior.  
 p.—posterior.  
 ep.—epiblast  
 mes.—mesoblast.  
 hyp.—hypoblast.  
 Pr. str.—primitive streak.

## ADDITIONS TO THE ERYSHIPHÆ OF ALABAMA.

BY GEO. F. ATKINSON.

In Vol. VII, II, of this Journal was published a list of the Eryshiphæ, collected by the writer, from the Carolinas and Alabama. During the following year several more species were collected in Alabama by the writer and one of his students. The former list was accompanied with quite full notes of a descriptive character. In the present list only such notes are added as seem necessary in addition to the characterizations found in descriptive works:

*Sporotheca castagnei* Lev.

On *Erectites hieracifolia*, Nov. 5, 91; and *Bidens frondosa*, Nov. 3, 91, B. M. Duggar, collector.

*S. lanestris* Hark.

On *Quercus alba*, Dec. 91, G. F. A. The conidial stage only was found.

*Erisiphe cichoracearum* D C.

On *Helianthus annuus*, Oct. 19, 91, B. M. D. *Aster tradescantia*, Nov. 31; *A. diffusus*, Nov. 30; *Mikania scandens*, Oct. 26. and *Solanum carolinense*, Nov. 10, 91, G. F. A.

*E. galeopsidis* D C.

On *Verbena urticifolia*, Oct. 23, 91, B. M. D.

*E. liriodendri* Schwein.

On *Liriodendron tulipifera*, Oct. 28, 91, B. M. D.

*Phyllactinia suffulta* (Reb.) Sacc,

On *Cornus florida*, Nov. 3; *Cornus* sp. undtd, Oct. 18.

*Podospæra biuncinata* C. & P.

On *Hamamelis virginiana*, Oct 28, 91, B. M. D.

*P. oxacantha* (DC).

*Prunus americanus* var. *mollis*, Oct. 31, 91, B. M. D; *Cratægus*, Nov. 9, D. H. Benton.

*Microsphæra semitosta* B. & C.

*Tecoma radicans*, Oct. 19, 91, G. F. A. This species has heretofore been reported only on *Cephalanthus occidentalis*. The perithecia are a little larger than those I have observed on *Cephalanthus*, measuring 90 to 115. The appendages in well matured specimens are very characteristic.

*M. euphorbiæ* B. & C.

On *Euphorbia preslii*, Oct. 21, 91, B. M. D.

*M. ravenelii* B.

On *Gleditschia tricanthos*, Oct. 13, 91, G. F. A.

*M. vaccinii* C. & P.

On *Vaccinium*, Oct. 18, 91, B. M. D.

*M. grossulariæ* (Wallr.).

On *Sambucus canadensis*, Oct. 13, 91, G. F. A. In the previous list this occurred as was given as *M. vanbruntiana* Ger.

The measurements are given in terms of the micromillimeter.

BOTANICAL DEPARTMENT, CORNELL UNIVERSITY.

## SOME SEPTORIÆ FROM ALABAMA.

BY GEO. F. ATKINSON.

The species of *Septoria* enumerated in this list were collected during my connection with the Alabama Polytechnic Institute at Auburn, Ala. The list is not large, perhaps from the fact that no especial effort was made to collect the members of the genus. Where no name is given as collector they were collected by myself. Where no locality is given Auburn should be understood.

*Septoria brunellæ* E. & H.

On *Prunella vulgaris*, July 16, 90, Shorters. The specific name of this plant was given from a mistaken spelling of the genus *Prunella* which has crept into many American botanical works. See Coville, Bot. Death Valley Expedition, p. 176.

*S. cerastii* Rob. et Desm.

On *Cerastium arvense*, Mar. 25, 91. Perithecia not very black, probably because they are not very old. The spores are a little stouter than the description calls for, and are faintly 1-5 septate. The spores in the

specimen in Roumg. Fung. Gall. Exs. 2485, are also faintly 1 – 5 septate; the perithecia are very black but agree with the Alabama specimens in being rather angular in outline.

*S. rubi* West.

On cultivated Rubus, Aug. 8, 90.

*S. rubi var alba* Peck.

On Rubus trivialis, Apr. 91, Mobile, Zimmer Bros. The leaves are also affected with *Cercospora rubi* West. and *Caeoma nitens*.

*S. virgauræ* Desm?

On *Solidago seratina*. There is some doubt about the correct determination of this plant. It seems near this species, but the spores measure 30 – 40 and are faintly 3 – 5 septate. Perithecia small 50 – 75. Spots small, whitish, depressed, dark bordered.

*S. erechtites* E. & E.

On *Erechtites hieracifolia*, Sept 10, 91, B. M. Duggar.

*S. ænothera* West.

On *Ænothera biennis*,

*S. dianthi* West.

On *Dianthus barbatus*,

*S. speculariæ* B. & C.

On *Specularia perfoliata*, Mar 28, 90.

*S. jussicæ* E. & K.

On *Jussiaea leptocarpa*, July 24, 91, Duggar and Newman.

*S. sambucina* Pk.

On *Sambucus canadensis*, Aug 24, 91, B. M. D.

*S. sonchinea* Thüm.

On *Sonchus oleraceus*, Feb. 25, 91, B. M. D.

*S. violæ* West.

*Viola primulæfolia*, July 16, 90, Shorters.

*S. xanthii* Desm.

On *Xanthium*, July 11, 90, Uniontown.

*S. graminum* Desm.

On *Panicum sanguinale*, Aug. 19, 91, B. M. D. Spots brown, elongate, irregular or involving the larger part of the terminal portion of the leaf. Perithecia amphigenous, more abundantly epiphyllous black, frequently depressed when dry, 80-90. Spores hyalines, slender, larger at base, soon tapering into a long, very slender, strongly curved flagellum, 2-10 septate. Very young ones are narrowly obclavate with the smaller end little curved and 1-2 septate, 1-1½ in diameter at base, 30-70 long.

*S. alabamensis* n. sp.

On *Nepeta glechoma*, Jan. 29, and Feb. 27, 91. Spots indefinite, occupying irregular portions of the leaf. Perithecia 80-90. Spores 20-30 x 1 or less, sometimes faintly 1-3 septate, straight or slightly curved or flexuous.

The measurements are given in terms of the millimeter.

BOTANICAL DEPARTMENT, CORNELL UNIVERSITY.

### ADDITIONAL NOTE ON THE FUNGI OF BLOWING ROCK, N. C.

In making out the list of fungi from Blowing Rock, which was published in Part 2, Vol. IX, of this Journal, two species were overlooked. They are as follows:

*Cordyceps acicularis* Rav.

On larva of elaterid beetle.

*Cnomoniella coryli* (Batsch.) Sacc.

On leaves of *Corylus*.

GEO. F. ATKINSON.

## AN EXAMINATION OF THE CHLORIDES OF ZIRCONIUM.

BY F. P. VENABLE.

A chloride of zirconium of definite composition would prove a valuable compound for determining the atomic weight of the element. There are several difficulties in the way of securing such a result:

1. The tendency to form basic chlorides.
2. The ease with which hydrochloric acid is lost through the action of heat and of dehydrating agents.
3. The presence of free hydrochloric acid.
4. The deliquescent nature of the chlorides.

It is particularly desirable that the conditions under which a definite chloride can be formed should be discovered, as zirconium seems to yield no very satisfactory compounds for the determination of the atomic weight. There have been many efforts at finding out these exact conditions.

Most text-books state that anhydrous, pure zirconium tetra-chloride can be prepared by passing dry chlorine over a mixture of charcoal and zirconia heated to a high temperature. Hermann used this sublimed zirconium chloride for the determination of the atomic weight. As Clarke says, however, little confidence can be placed in his results. Bailey\* has recorded that even with great care to avoid the presence of moisture, he was unable to prevent the formation of oxychlorides. He also says that in no case was it found possible to prepare the chloride free from iron and silica. The

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\*Chem. News. LX., 17.

necessity for the presence of these in the materials used or in the resulting compound is not very apparent. I have as yet had no opportunity of repeating his experiments.

The chlorides most commonly worked with have been those formed by the solution of the hydroxide in hydrochloric acid, followed by precipitation or crystallization from concentrated hydrochloric acid.

Berzelius attempted to remove the excess of hydrochloric acid by heating the salt to  $60^{\circ}$  C. but was not able to obtain a definite compound. Two analyses gave:

ZrO <sub>2</sub>	0.332	0.485
AgCl	0.661	1.076

The silver chloride should be about two and one-third times as much as the oxide.

Paykull dried the salt between filter paper and found the composition of the crystals to be ZrOCl<sub>2</sub>. 8H<sub>2</sub>O, the amorphous form precipitated by hydrochloric acid being 2ZrOCl<sub>2</sub>. 13H<sub>2</sub>O.

Endemann has described basic or oxychlorides Zr<sub>3</sub>O Cl<sub>4</sub>; ZrOClOH, and Zr<sub>8</sub>O<sub>8</sub>Cl<sub>7</sub>(OH)<sub>9</sub>; Troost and Hautefeuille have described others, Zr<sub>2</sub>O<sub>3</sub>Cl<sub>2</sub> and Zr<sub>2</sub>OCl<sub>6</sub>. In fact water is so easily taken up and hydrochloric acid lost that a large number of such indefinite compounds might be prepared by slightly varying the conditions.

Nylander\* made a series of attempts at dehydrating the chloride. He prepared the chloride by dissolving the hydroxide in hydrochloric acid and evaporating to crystallization. The salt formed white needles, easily

\*Bidrag till k annedomen om Zirkonjord. Inaug. Diss. Lund 1864.

soluble in water. They were washed with alcohol and for analyses I. and II. were pressed between filter paper. III. and IV. were dried over sulphuric acid. The results were as follows:

Zr	27.56	95.69	30.11	31.78
Cl	21.58	21.58	23.06	23.80
Loss (H <sub>2</sub> O)	50.86	52.78	46.83	44.12

or calculated on a dry basis:

Zr	56.08	54.41	56.63	57.18
Cl	43.02	45.59	43.37	42.82

Again preparations were made as before. I. was dried between filter paper, II. over sulphuric acid, III. was pressed between filter paper and then dried over sulphuric acid, IV. was dried a long time over sulphuric acid. The analyses gave the following:

Zr	28.52	34.91	37.78	35.69
Cl	21.93	26.09	25.87	21.74
Loss	49.55	39.10	36.35	42.57

or calculated on a dry basis:

Zr	56.93	57.23	59.34	62.14
Cl	43.07	42.77	40.66	37.86

Lastly he allowed a solution of the chloride to evaporate over sulphuric acid, washed the crystals obtained with alcohol and pressed them between filter paper. Analyses gave:

	I.	II.
Zr	27.94	28.74
Cl	27.32	26.67
Loss	44.74	42.62

or, calculated on a dry basis:

Zr	50.36	50.04	Zr	38.50
Cl	49.44	49.96	Cl <sub>4</sub>	61.50

The above results show that his preparations were indefinite oxychlorides or mixtures, in varying proportions of zirconium tetrachloride and oxychloride.

Bailey repeatedly crystallized the chloride from hydrochloric acid, washed it with hydrochloric acid and then removed the free acid.

1. By washing with a mixture of one part alcohol and ten parts of ether.

2. By gently heating the salt.

3. By exposing the finely divided salt at ordinary temperatures in a vacuum desiccator over potash, until no hydrochloric acid appeared when air passed over it.

The analysis was performed by dissolving the salt in water and precipitating the zirconia with ammonia, then acidulating with nitric acid and precipitating the chlorine by means of silver nitrate. By method 2 a constant and progressive diminution of chlorine was observed. Therefore no analyses were made. For the other methods he gives the results of the analyses by a statement of the ratio of ZrO<sub>2</sub> to AgCl:

	ZrO <sub>2</sub> : AgCl
Berzelius's determination	1 : 1.991
	1 : 2.260
Bailey's method 1:	1 : 2.206
	1 : 2.179
	1 : 2.226
	1 : 2.260
Method 2:	1 : 2.264
Method 2 without washing:	1 : 2.245
	1 : 2.309
	1 : 2.285
ZrOCl <sub>2</sub>	1 : 2.350

These preparations are evidently mixtures also.

Hermann\* states that the hydrated chloride, gotten in crystals on evaporating its aqueous solution, becomes opaque at 50° C., giving off part of the water and half of the hydrochloric acid, and leaving a basic chloride or oxychloride,  $ZrCl_4 \cdot ZrO_2 \cdot 18H_2O$  or  $ZrOCl_2 \cdot 9H_2O$ . The same compound is obtained in stellate groups of white silky prisms on evaporating a solution of the chloride. These crystals, when heated, become white and turbid and are converted into the anhydrous dioxychloride  $ZrCl_4 \cdot 2ZrO_2$ .

The conditions here are inexact, and though Hermann may have obtained these compounds, he would find it difficult to prepare them again. While it is perfectly true that an oxychloride is formed on the evaporation of an aqueous solution of the chloride, I have been unable to obtain the compounds he mentions. Linne-mann† maintains that crystallization from hydrochloric acid (sp. gr. 1.17) and treatment with alcohol and ether gives a fine, crystalline, snow white, silky body, leaving 50 per cent. of its weight on ignition, and therefore very nearly pure  $ZrCl_4$  which should leave 52.5 per cent. He claims that this is "chiefly a neutral, not a basic compound."

My own experiments on the dehydration of this salt have extended over the past two years, as opportunity was afforded. Several series of experiments were undertaken; some along the lines attempted by others, and others by methods not tried before. In all the purified chloride, obtained by repeated crystallization from hydrochloric acid was used, the salt being still wet with

\*Watts Dict. V. p. 180.

†Chem. News. LII. 224.

the excess of the acid. There was no attempt at drying this between filter paper. The method of preparing this salt has been fully described in a previous paper in the *Journal of Analytical and Applied Chemistry*, 5, 551.

In the first experiment this chloride was washed once with water and then put in a dessicator and dried over calcium chloride (porous dessicated). It remained in the dessicator about seven months. Even after this lapse of time it still continued to show a slight loss in weight. It yielded, on analysis, 48.84 per cent.  $ZrO_2$ .

Another portion was placed in a jar over solid lumps of sodium hydroxide. After six weeks the loss was very slight. Careful ignition left a residue of  $ZrO_2$ , equivalent to 42.99 per cent. of the original weight. There was found to be 24.44 per cent. of chlorine present.

Again a portion was placed over calcium chloride and dry air was drawn over it at the rate of about fifty litres in the twenty-four hours for six months. After the first two months it was examined weekly by the interposition of a flask containing silver nitrate to see whether hydrochloric acid was still coming off. Even after the lapse of so long a time as this it was found that the loss of hydrochloric acid continued, although it was slight. On analysis this gave  $ZrO_2$  42.28 per cent. and Cl. 24.35. Although the results in this, and the experiments immediately preceding, correspond fairly well they are unsatisfactory, as they point either to a mixture of chlorides or an oxychloride of very complicated formula, and hence unsuited for the ultimate aim of the research.

Lastly a portion was placed over concentrated sulphuric acid and the atmosphere above it exhausted occa-

sionally. This was kept up during two months of summer weather. The loss in the last fifteen days was about .02 per cent. of the whole. The mass was powdery, with a slightly discolored crust. It was all soluble in water, however, and yielded a clear colorless solution. It contained 53.30 per cent of  $ZrO_2$ . This corresponds very nearly to the formula  $ZrCl_4$  and is altogether at variance with the results obtained by Nylander and with the assertion made by Hermann, that half of the hydrochloric acid was lost over sulphuric acid.

This last experiment showed the possibility of securing pure zirconium chloride, provided the excess of hydrochloric acid could be removed. It was thought that this might be done by heating in an atmosphere of hydrochloric acid. A weighed flask was so arranged that it could be kept at a definite temperature while a stream of dry hydrogen chloride was passing through it. The temperature ranged from  $100^\circ$  to  $110^\circ$  C., and the chloride placed in the flask melted, solidifying again after the loss of the water and excess of hydrochloric acid. If the drying was done slowly enough fine crystals of zirconium chloride were gotten which lost no further weight on being kept at  $100^\circ$  C. A more rapid drying left a hard white mass which was quite hygroscopic. Heating this mass for several days did not cause any diminution in weight, provided the flask was kept full of hydrogen chloride. If the mass was heated even a short time in the absence of hydrogen chloride then further heating caused a continuous loss of weight even in the presence of a rapid stream of hydrogen chloride. After this it was impossible to secure a constant weight.

This method of drying has been tried repeatedly on

various preparations, and I regard them as showing conclusively that a neutral chloride of zirconium can be prepared and dried.

Analyses of this chloride gave the following percentages of  $ZrO_2$ :

52.70

52.78

52.63

Experiments have already been begun with a view of utilizing this body in a series of experiments looking to a revision of the atomic weight of zirconium.

In connection with this subject it may be well to mention some improvements in the method of purifying zirconium chloride. (See *Journal of Analytical and Applied Chemistry*, 5, 551).

In the first place the separation from silica by evaporation to dryness is not complete. It is impossible to heat this chloride to the necessary temperature without such a decomposition as will render the zirconium chloride also insoluble. It is best then to make this preparation as thorough as possible by heating, then to change the chloride into oxide by ignition, and to treat this several times with hydrofluoric acid until the trace of silica is all driven off. This silica is too small in amount to interfere with ordinary uses but would have to be removed where perfect purity was demanded.

Again, where the hydroxide is dissolved in dilute hydrochloric acid, or contained so much water that the acid was greatly diluted by it, it will be found that more or less of a white insoluble powder will form on evaporation as recommended on a water-bath and on subsequent treatment with boiling strong hydrochloric acid. By a careful arrangement of glass wool in a hot water funnel the dissolved chloride can be filtered

away from this soluble mass. It seems to be quite insoluble in hydrochloric acid though easily dissolved by water. Analysis shows that this mass is  $ZrOCl_2$  and with it was found as an impurity whatever silica the separation by heating failed to remove.

Lastly, my assistant, Dr. Baskerville, has shown that much time and hydrochloric acid will be saved if in the solution containing much iron the zirconium hydroxide be first precipitated out by means of sulphur dioxide. This precipitate can then be dissolved in acid and purified by crystallization as already recommended.

Of course it need scarcely be mentioned that if silica has been removed by ignition and treatment with hydrofluoric acid, it will be necessary to fuse once more with caustic alkali and repeat the ordinary purification.

UNIVERSITY OF NORTH CAROLINA.

## SOME ATTEMPTS AT THE FORMATION OF ETHYL GLUCOSIDE.

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J. R. HARRIS.

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Glucosides are substances occurring in nature in plants and are supposed to be ethereal derivatives of the glucoses. Under the action of dilute acids or ferments they break up into glucose and other bodies. A number of these ethereal derivatives of glucose can be prepared synthetically in the laboratory.

A. Michael<sup>1</sup> obtained them by the action of alcoholic solution of acetochlorhydrose upon the alkali salts of phenol.

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1. Compt. rend. 89, 355.

The formation of Helicin according to the following equation would be an example of this method:  $C_6H_7ClO_5(C H_3O)_4 + C_7H_3O_2K + 4C_2H_5O = C_{13}H_{16}O_7 + KCl + 4C_2H_5C_2H_3O_2$ .

Emil Fischer<sup>2</sup> has recently discovered a new method of forming these derivatives, and has prepared compounds of methyl, ethyl, propyl, amyl, isopropyl, allyl and benzoyl glucose. Also analogous compounds of arabinose, methyl-arabino-side.

These do not reduce Fehling's solution; they break up into glucose and the corresponding alcohol on treatment with dilute acids or ferments, and behave in every way similarly to the natural glucosides.

I proposed to form them by the action of alkyl iodide upon the sodium glucosate according to the following equation:



For this experiment, the ethyl glucoside was chosen, as the materials for its preparation were already on hand, and because in all probability the method would work as well for this one as any other member of the series.

The insolubility of sodium glucosate in all neutral anhydrous mediums on hand, was recognized at the outset of this work to be a great obstacle in the way of the successful operation of the method.

As a preliminary test, 15 grs. of anhydrous glucose was taken and gently boiled for some time with 150 c. c. of about 97 per cent. alcohol. This solution, when saturated, was poured off into a large flask in which the precipitation was to be made, and kept warm by standing in a water bath, in order to prevent the glucose from crystallizing.

2. Ber. 26, 2400.

Another portion of 150 c. c. of alcohol was poured upon the residue and gently boiled as before. When the hot alcohol seemed no longer to have any solvent action upon the residue, it was carefully decanted off into the precipitating flask.

About half the amount of glucose taken went in solution by this treatment.

The alcoholic solution was then precipitated with an excess of sodium alcoholate, and allowed to stand over night. An amount of ethyl iodide equivalent to the sodium alcoholate used was then added direct to the alcoholic solution containing the suspended precipitate of sodium glucosate. The mixture was now gradually warmed up on a water bath, with a reflux condenser attached to prevent loss of ethyl iodide.

At about  $75^{\circ}$  C. the mixture began to deposit a reddish brown substance upon the bottom of the flask, and the solution to change to yellow color. At about  $80^{\circ}$  C. the mixture boiled, and the deposition on the bottom of the flask was more rapid, it being complete in about twenty minutes, leaving a dark brown supernatant liquid. A portion of the liquid was taken out and allowed to stand for some time over freshly ignited potassium carbonate, but no absorption of iodine was noticed.

This, and the remaining portion in the flask, was then filtered through animal charcoal. A liquid of a pale brown color was obtained, which reduced Fehling's solution.

It was not thought that the change would be complete, so it was impossible to tell by this means whether or not the glucoside had been formed. It was then evaporated in a water bath to a syrupy consistence, and the syrup extracted several times with acetic ether.

The acetic ether extract was evaporated in a dessicator over sulphuric acid.

By this means beautiful crystals were obtained, however, colored somewhat by the brownish syrup.

These crystals were tested by the flame test for sodium, and starch paste for iodine. They were clearly shown to be sodium iodide.

The glucose used in this experiment was thought to be impure, and besides it was probable that another test, under somewhat different conditions, would give more satisfactory results.

In his work on glucosides, Fischer<sup>3</sup> dissolves the glucose in a little water, and besides, water is formed in the reaction which he made use of, hence I concluded that it was not absolutely essential for the materials used to be water free. I accordingly started another experiment, using pure anhydrous glucose<sup>4</sup> of my own preparation dissolved in a little water.

Fifteen grams of glucose was dissolved in 5 c. c. of hot water and the solution added to 300 c. c. of 98 per cent. alcohol. This solution was precipitated by an equivalent amount of sodium alcoholate. The precipitate was rapidly filtered off by means of a pump, exposed to air as little as possible, washed with 98 per cent alcohol and transferred to the precipitating flask.

The precipitate was now suspended in 300 c. c. 98 per cent alcohol and an amount of ethyl iodide added equivalent to the sodium ethylate. The mixture was now carefully heated up on a water-bath, with frequent shaking.

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3 Ber. 26, 2400.

4. Made by the method of Soxhlet J. pr. ch. 21, 245, as given in Emil Fischer's book on Organic Preparations, and purified by recrystallization from strong alcohol.

It was noticed that the change began to take place as before, at about  $70^{\circ}$  C., by the brownish deposit at the bottom and sides of the flask, as the flask was this time immersed in hot water, taking care that the mixture should not come to boiling.

The greater portion collected on the bottom as a dark brown semi-syrup at that temperature, and the supernatant liquid was straw colored.

The change was complete on heating for 30 minutes just below the boiling point of the mixture. The liquid in the flask now had a strong smell of ethyl iodide, and reduced Fehling's solution.

About half was poured into a smaller flask provided with a reflux condenser and gently boiled in a water bath for three hours. At the end of this time the smell of the ethyl iodide did not seem to have diminished, and it still reduced Fehling's solution.

It was then evaporated on a water bath to a syrupy consistency, and the syrup extracted with a mixture of equal parts alcohol and ether, benzen, petroleum ether and acetic ether. No crystal of sodium iodide could be obtained, and only a thick syrup which powerfully reduced Fehling's solution.

The other portion of the liquid was then transferred to a distilling flask and fractioned. A few c. c. came over between  $74^{\circ}$  and  $78^{\circ}$  C. and was mainly  $C_2H_5OH$ . Most of the alcohol comes over between  $78^{\circ}$  and  $82^{\circ}$  C., leaving a dark brown syrup behind in the flask. The dark brown substance obtained as a deposit in the operation was set aside for examination. Meanwhile another experiment was started, varying the conditions somewhat.

Fifteen grams of anhydrous glucose was dissolved in 400 c. c. boiling absolute alcohol. The solution

cooled somewhat, and an equivalent amount of sodium ethylate added, and rapidly cooled to the same temperature. The precipitate was filtered off by means of pump and washed with absolute alcohol, avoiding all exposure to the air possible. It was then transferred to the precipitating flask and an equivalent amount of ethyl iodide added.

The mixture in the flask provided with a reflux condenser, was gradually warmed up to boiling. The changes first noted were the formation of a dark brown deposit on the bottom of the flask at about  $70^{\circ}$  C., a coloring of the liquid, and at the same time a diminution of the precipitate. Finally, at the boiling point of the mixture, the precipitate appeared to become sticky, and to collect into one mass, instead of being flocculent, and to gradually get smaller and smaller, both going into solution and coloring it a dark brown and melting down to a semi-syrup on the bottom of the flask.

The, time, in this test, for the change was one hour; much longer than in the former experiments. The liquid in the flask was divided into two portions, one of which was boiled in a flask with a reflux condenser for several hours, and no change was observed.

It reduced Fehling's solution and had a strong smell of ethyl iodide. The portions were now combined and submitted to fractional distillation.

About half of the amount of ethyl iodide used was recovered in the fraction coming over between  $74^{\circ}$  and  $78^{\circ}$  C.

The alcoholic fraction emitted still a strong smell of the iodide. Hence it seemed that the ethyl iodide had played no part in the change undergone by the sodium glucosate. The residue left in the flask from the experi-

ment was treated with benzen, ether, petroleum ether and chloroform, but none of these had any appreciable solvent action. It was then dissolved in water, a portion of the solution evaporated to dryness in a platinum dish, dried to constant weight, and then ignited at a low red heat.

Weight of dish and substance,	- -	24.9115 gr.
Weight of dish,	- - - - -	23.8732

Weight of substance taken,	- -	1.0383
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Weight of ash and dish,	- -	24.1276 gr.
Weight of dish,	- - - - -	23.8732

Weight of ash,	- - - - -	2644
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To ash, 34.50 per cent.

This was recognized as sodium carbonate, and is equivalent to 10.63 per cent sodium.

The percentage of sodium calculated for sodium glucosate is 11.37 per cent.; found in this syrup 10.63 per cent. Hence it must be a modification of glucosate.

In conclusion it is hardly necessary to say that the negative results of the above experiments do not prove the impracticability of the reaction proposed. It remains, however, to find some neutral anhydrous medium in which sodium glucosate is soluble and by which it is not decomposed, as in most chemical reactions of this character the reacting bodies must be either liquid or in solution.

ON THE GEOLOGICAL HISTORY OF CERTAIN TOPOGRAPHICAL FEATURES EAST OF THE BLUE RIDGE.

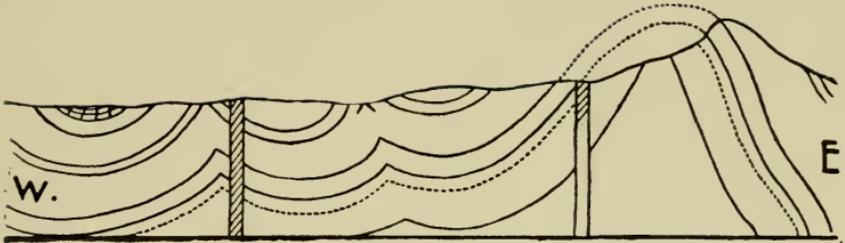
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COLLIER COBB.

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The peculiar forms of the topographic outliers of the Blue Ridge, extending across North Carolina from King's Mountain on the south to Pilot Mountain on the north, attracted my attention when a boy, and in May, 1892, I visited the region and began a study of the King's Mountain district under the direction of Professor N. S. Shaler. The entire summer was spent on the field, as well as the larger portion of the following summer and two of my winter vacations.

The precipitous faces of the mountains, lying at two well-marked levels, suggested to me wave action, and I began my work upon the hypothesis that these outliers had been islands in a sea of no great depth, at a date comparatively late, when the age of the rocks composing the mountains is taken into consideration. The accompanying geological section, from what was formerly known as Bird's Quarry, in the present village of King's Mountain, westward across the mountain, I have adapted from Lieber, putting in the quartzite which forms the crest of the mountain, lying above Lieber's "mica slate." The order of succession of these rocks is, beginning with the newest, limestone, talc-schist, a white sandstone passing into a slightly flexible variety, micaceous shale, diorite-schist, talc-schist, quartzite, and micaceous shale, the last resting on a granitic rock which outcrops on Crowder's creek at the eastern foot of the mountain.



SECTION EAST AND WEST THROUGH KING'S MOUNTAIN.

[There is a marked unconformity between the limestones and the schists not shown in Lieber's section.]



King's Mountain, Crowder's Mountain, and the hills to the north on the old Lincolnton road, are the western members of a southward plunging syncline while the hills to the east of High Shoals, Dallas and Gastonia, are the eastern members, the same hard crest making the crest of them all. On the eastern side of the syncline the dip to the west is not great, averaging not more than fifteen degrees; while the eastward dip on the King's Mountain side is usually between thirty degrees and forty-five degrees. The eastern hills are low, rising very little above the surrounding country, which varies little from nine hundred feet above tide, and they show none of the topographic features so prominent on the western side, where King's Mountain rises to a height of 1692 feet, and Crowder's Mountain 1606 feet. The level of nine hundred feet is a base-level of erosion, clearly marked, and extending entirely across the State, from north to south, and just above "the fall-line" to the base of the Blue Ridge mountains.

The evidences of wave action upon and at the base of these cliffs is clear and unmistakable. They consist of sea-caves, pinnacled rocks—many of the Devil's Pulpit type—washed-out dykes, crevices of the spouting horn sort, below which may even yet be made out the old beaches which lay below the cliffs. These wave-markings are shown in the photographs of various portions of King's and Crowder's mountains. These features are nearly all on the west side, the side away from the dip. The best marked of these old sea-benches varies little from 1400 feet above sea-level. The next one that can be made out distinctly at all points is about 1000 feet above sea.

I then made a search for the fragmental material that

had accumulated during the island existence of these mountains. There is a good talus all around, rather more on the eastern side, where it is shingly, than on the west. A search for the stratified deposits immediately around the mountains was not at first so successful; but in the cut of the Charleston, Cincinnati and Chicago railroad, at Blacksburg, S. C., just back of the Cherokee Inn, is a very good exposure showing two or three feet of quartzite pebbles covered with about the same thickness of mottled clay closely resembling the Miocene clays of eastern North Carolina. Later, I found the same strata of quartzite pebbles and clays in the old cutting at the Catawba Gold Mine, about one mile from the mountain, and also pebbles, clays and regular stratified sands in a basin like region on the road from All Healing Springs to Gastonia, two miles southwest from Gastonia. The general absence of these deposits, however, is to be explained by their looseness, and the ease with which they could be washed away by the currents. The taluses have in every case, I think, been formed since the sea departed from the region, as the materials composing them are angular fragments, and never the round pebbles to be found in the deposits mentioned above. Not only have the deposits of this time been largely washed away, but the older crystallines, which are here decayed to great depths, have yielded readily to the rains wherever the land has been deforested. The accompanying photograph, taken on the Gastonia road two and a half miles from All Healing Spring, shows a gully twenty to thirty feet deep made by the rains since the Civil War when the field was abandoned. It may be noted that the trees which have come upon the field since its

abandonment are none of them more than thirty years old, as shown by their rings of annual growth.

I could find in the King's Mountain region no means of determining the approximate age of these deposits, but when I extend my observations across the State to the Dan River and Pilot Mountain regions, I found there the same pebbles of quartz and quartzite resting unconformably upon the brown sandstones of the Newark system, while above the pebble-beds, and conformable with them, were the same mottled clays that I had found in the King's mountain region. This established their date as certainly post-Triassic, and I should have been inclined to call them Cretaceous, had not an examination of the border of the Cretaceous in Harnett, Cumberland and Moore counties, convinced me by the coarseness of the materials there that there was the western border of the Cretaceous, and that the beds of that age could not have extended as far westward as the region under consideration. It led me to the belief, however, that the base-levelling of the piedmont region must have been accomplished while the shore-line lay near the present western border of the Cretaceous rocks, or in Cretaceous time. And, while I am as yet unable to determine the exact age of these deposits, I have at least found out that the peculiar shaping of these topographic outliers was the work of waves, and that it was accomplished in post-Cretaceous time.

## DO SNAKES CHARM BIRDS?

COLLIER COBB.

On the 15th of May I happened upon an interesting thing which throws some light on the alleged power of snakes to charm birds. A few days before this, a snake, a garter, (*Eutaenia*), about the size of a man's finger and little over eighteen inches in length, had been killed in the walk leading from the New East Building to the eastern side of the University campus, at Chapel Hill. The head of the snake had been pushed into the hole made by the end of the cane with which it was killed, and the snake was in this position with its head pressed down in the hole, when I came upon it, surrounded by seven quails (*Ortyx virginiana*). The quails were gazing upon the snake, very much as "charmed" chickens will gaze upon the chalk line or the crack in barn floor, taking no notice whatever of my presence until I lifted the snake up with a stick. They remained in the position in which I found them long enough for a boy to run from the Episcopal church to the walk, which must have taken two or three minutes. This observation is valuable as showing that, in this instance at least, the "charming" is in the bird itself, and is not a power possessed by the snake.







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