We propose in the near future to see that a thorough test of the apparatus is made, taking account of all known sources of error, and we have reason to hope that the results so obtained will compare with the best of the older investigators.

STANFORD UNIVERSITY,
May 17, 1904.

THORIUM; CAROLINIUM, BERZELIUM.[1]

BY CHARLES BASKERVILLE.

Received June 24, 1904.

SYNOPSIS.

THIS paper presents a brief historical account of the discovery of thorium and the questions raised as to its elementary character.

The published evidence is considered in conjunction with experimental data obtained and the conclusions arrived at that thorium is not a primary radioactive body.

The complex nature of thorium is proved by the conduct of salts with certain organic bases, as phenyl hydrazine, for example. Fractions were had, giving atomic weights from 212 to 252, the original being 232.5.

Pure thorium oxide from several sources was converted into the chloride by heating it, mixed with pure sugar carbon, within quartz tubes during the passage of dry chlorine. A volatile chloride, "weisser dampff" of Berzelius, was obtained decreasing in amount according to the duration and temperature of the reaction. The purified, delicately green oxide obtained from this gave a specific gravity of 8.47 and the element, berzelium, an atomic weight of 212 (tetrad).

The temperature of the porcelain tube was raised and thorium tetrachloride distilled away. The residue in the carbon boat on purification gave a grayish pink oxide with a specific gravity of 11.26 and an atomic weight of (tetrad) 255.6 (carolinium). The new thorium, or that in a large measure freed from the berzelium and carolinium, gave an atomic weight of 220.6 and a white oxide with a specific gravity of 9.2. The original thorium gave atomic weights 232.5 to 232.6 and its oxide had a specific gravity of 10.5.

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[1] Presented before the New York Section of the American Chemical Society, April 8, 1904.

The original thorium dioxide phosphoresces under the influence of ultraviolet light, as does zirconium dioxide. Berzelium and carolinium oxides do not respond to this stimulus, while the new thorium glows with increasing luminosity, according to the decrease of the novel substances.

All these bodies are radioactive.

Certain chemical differences are noted, as, for example, the conduct of their salts with organic bases, fumaric acid, etc. Carolinium oxide is soluble in concentrated hydrochloric acid, while berzelium and thorium oxides are not.

Spectral data are wanting, in fact, the limited portions of the spectra (arc and spark) mapped show the bodies identical. The materials are not yet sufficiently pure, nor the spectral data sufficiently complete, to warrant final acceptance, although the preponderance of evidence is favorable to the assumption of the existence of two new members of the family of chemical elements.

The marvelous phenomena of radioactivity, accounts of which have filled our chemical and physical literature for the past six years, have stimulated numerous investigators to take part in asking a solution which would be satisfactory and not wholly drive us from our former conceptions of the fundamental laws of the conservation of matter (whatever it may be) and energy (however we may measure it). Naturally such have had to do with thorium, the radioactivity of which was independently noted by G. C. Schmidt[1] and Curie,[2] and studied extensively from both points of view by Rutherford, Soddy and their co-workers,[3] Giesel,[4] Hofmann and Zerban,[5] Owens,[6] Pegram[7] and others, as well as myself.[8]

Other communications upon our researches on thorium have been withheld in the hope of early reaching a solution of the difficult problems involved in an investigation of that element. While the work is far from complete—is any scientific work com-

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[1] *Wied. Ann.*, **65**, 141 (1898).

[2] *Compt. Rend.*, **126**, 15; see also Mme. Curie's Thesis, presented to the Faculté des Sciences de Paris, 1902.

[3] Many papers in *Phil. Mag.*: *Proc. Chem. Soc.*, **18**, 2 (1902), and Transactions, **81-82**, 476 (1902), etc.

[4] *Ber. d. chem. Ges.*, **34**, 3776 (1901).

[5] *Ibid.*, **35**, 533 and 1457 (1902), and **36**, 3093.

[6] *Phil. Mag.*, October, 1899.

[7] *Phys. Rev.*, **17**, 424 (1903).

[8] This Journal, **23**, 761 (1901).

plete?—we think sufficient evidence of the complexity of the element has been accumulated to warrant definite statements and excuse us from having had recourse to that "bastard *a priori* method," according to Herbert Spencer, namely, drawing conclusions from insufficient data. Further, on account of the numerous investigations that are coming out upon the elements of high atomic weights it is well to offer our observations that they may be of service to others.[1]

In 1817, Berzelius,[2] while investigating gadolinite from Korarfvet and another mineral from Finbo, believed he found an unknown oxide similar to zirconia and called it "Thorine," after the mythological Scandinavian god of thunder, Thor. This master chemist, marvelously accurate, especially for the time, soon learned[3] that "thorine" was in fact a phosphate of the yttrium earths and the name properly remained but a short time in chemical literature. In 1828 this same chemist[4] found a new mineral, thorite, on the Island Lövö, near Brevig, Norway. In it he discovered a new element with which he revived the name, thorium: Chydenius[5] completed the investigation and Cleve[6] revised the

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[1] NOTE—When my first preliminary paper on the complexity of thorium was made known publicly, in a note I gave as an excuse for publishing the work a statement of the fact that I had written Professor Bohuslav Brauner that I thought I had brought about a breaking-down of the element. I requested a sample of the very pure body he had prepared and used in his excellent atomic weight determinations, that I might check my work. I received no acknowledgment of the letter and would not know to this day that it had been received but for what followed. Dr. Brauner shortly published some work which clearly pointed to thorium being composite. Having devoted some years of study to the work myself and following entirely different lines, I immediately, within eight days, at the first public opportunity, presented my paper. For fear I might be misunderstood, the facts outlined above were made known. In a letter to the editor of the *Chemical News*, Dr. Brauner took exception to my statement, assuming an intimation on my part that he had taken advantage of information contained in a private letter. The letter in which I gave no details of the method of procedure was quoted from (so it *was* received); furthermore an excuse was given for not having replied to the letter, that I was interfering with his field. Apparently a large number have interfered with that field since my publication. I purposed saying nothing regarding Professor Brauner's letter, but on account of the earnest solicitation of many friends the above statements are made known. It was utterly foreign to my mind to cast any reflections upon Professor Brauner. I appreciate most keenly his beautiful researches carried out in the rare earths in which field that savant ranks as a master. I must object, however, to his having the field reserved. In fact, our work was carried out upon entirely different lines and similar conclusions reached. While it is only human that one should care to have his work appreciated, yet I am not engaged in scientific work for the credit alone.

[2] "Afhandl. i. Physik. Kemi. och Mineralogie," Vol. V, p. 76; *Ann. chim. phys.*, **5**, 8; Schweigger's *Jour.*, **21**, 25.

[3] "K. Vet. Acad. Handl.," Vol. II, pp. 4, 315; J. B. Berz., **5**, 112 (1824).

[4] "K. Sv. Ver. Akad. Handl.," 1829, p. 11; *Ann. Phys.*, **16**, 388.

[5] "Kemisk undersökning of Thorjord och Thorsalter. Helsingfors, 1861, *Ann. Phys.*, **119**, 43.

[6] *Bull. Soc. Chim.* (2), **21**, 116 (1874).

older data in 1874. Nilson, with Krüss and Hillebrand, in many researches, determined its atomic weight and secured unquestionable evidence as to its quadrivalence.[1] Quite recently Wyrouboff and Verneuil,[2] for reasons we need not enter into here, brought up the question of the quadrivalence of thorium which really depended largely upon the specific heat values obtained by Nilson.[3] Biltz[4] appears to have settled the matter by a rigid examination of the thorium acetylacetonate of Urbain.[5]

In 1851 Bergmann[6] claimed to have found the oxide of a new element, "donarium," in the yellow variety of thorite, orangite, studied independently by himself and Krautz.[7] Damour,[8] the year following (1852), showed that donarium oxide was impure thorium oxide containing lead and uranium. Bergmann[9] shortly after observed that donarium and thorium were the same. Berlin[10] arrived at the same conclusion, as did Delafontaine in 1863.[11]

Again in 1862 was thorium mistaken for a new element, namely, wasium, reported by Bahr[12] in wasite from Rönsholm. The properties were very similar to those of thorium. Its existence not being clearly defined, Nicklès[13] investigated it, maintaining that it was a mixture of yttrium earths containing didymium and terbium. Delafontaine[14] insisted that it was a mixture of cerite earths and Popp[15] asserted that it was nothing else than yttrium containing cerium. The discoverer[16] shortly announced its identity with thorium and proved its hypothetical existence.

There are not a few instances in the history of chemistry where scientific interest in some particular element or compound has been stimulated directly or indirectly through its commercial application and the demand thereby created. This is particularly

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[1] *Ber. d. chem. Ges.*, **9**, 1056 (1876) : **15**, 2519, 2521, and 2537 (1882) ; **16**, 153 (1883) ; **20**, 1665 (1887) ; *Ztschr. phys. Chem.*, **1**, 301 (1887) ; etc.

[2] *Bull. Soc. Chim.* (3), **21**, 118 (1899).

[3] *Ber. d chem. Ges.*, **16**, 153 (1883).

[4] *Ann. Chem.* (Liebig), **331**, 334 (1904).

[5] *Bull. Soc. Chim.* (3), **15**, 347 (1896).

[6] *Ann. Phys.*, **82**, 561 (1851).

[7] *Ann. Phys.*, **82**, 568 ; *Ann. Chem.* (Liebig), **80**, 267 (1851).

[8] *Ann. Phys.*, **85**, 555 ; *Ann. Chem.* (Liebig), **84**, 237 (1852).

[9] *Ann. Phys.*, **85**, 556 ; *Ann. Chem.* (Liebig), **84**, 239.

[10] *Ann. Phys.*, **85**, 556, and **87**, 608 ; *Ann. Chem.* Liebig), **84**, 238 (1852).

[11] *N. Arch. Phys. Nat.*, **18**, 343 ; *Jahresber.*, 1863, p. 197.

[12] "Oefvers of K. Vet. Akad. Förhandl.," 1862, p. 415 ; *Ann. Phys.*, **119**, 572.

[13] *Compt. Rend.*, **57**, 740.

[14] *N. Arch. Phys. Nat.*, **18**, 369 ; *Jahresber.*, 1863, p. 201.

[15] *Ann. Chem.* (Liebig), **131**, 364.

[16] *Ibid.*, **132**, 227 (1864).

true of thorium. The first German patent issued Auer von Welsbach[1] marks the creation of unusual interest in the main constituent of his mantle. The improvement in the methods for its extraction on a large scale soon opened the gates wide for numerous researches. Although defined with precision through the work of those mentioned, Nordenskjold,[2] Petterson,[3] Troost and Ouvrard,[4] Berlin,[5] Delafontaine,[6] Bakhuis-Roozeboom, Urbain, Jannasch, Brauner, Kosmann, Chavastelon, Muthmann, Locke, Dennis, Matignon, Böttinger, Moissan, and many others,[7] yet the anomalous conduct of certain of its compounds has caused serious questions, by several investigators, as to its elementary nature.

Chroustchoff[8] reported an element associated with thorium in certain zircons and American monazite sands. Although little information is to be had as to this work, apparently the atomic weight, 220, was attributed to the element, which was detected spectroscopically. As Crookes remarks, "the spectrum of thorium is even more complicated than that of iron," hence further data are necessary. Auer von Welsbach[9] insists that thorium is complex.

In 1898, as adverted to, G. C. Schmidt[10] and Madame Curie[11] independently noted the radioactivity of thorium obtained from Bohemian pitchblende. Not long after the announcement of the Becquerel[12] rays, Crookes[13] showed that by fractioning uranium nitrate with ether, compounds could be obtained which did not affect the photographic plate. This indicated the separation of a new substance (Uranium X) and that radioactivity was not an inherent property of the element uranium, as maintained by Mme. Curie.[14]

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[1] *Monatsh. Sci.* (Quesneville) (4), **8**, 2 (1894) ; Patent List, p. 136, etc.

[2] *Jahresber.*, **13**, 134.

[3] *Compt. Rend.*, **91**, 232.

[4] *Ibid.*, **102**, 1422.

[5] Pogg. *Ann.*, **119**, 56 (1863).

[6] *Ann. Chem.* (Liebig), **131**, 100 (1864).

[7] Vide the excellent "Index to the Literature of Thorium," Joüet, Smithsonian Miscellaneous Collections, No. 1374.

[8] *J. russ. phys. Chem. Ges.*, **29**, 206 ; *Chem. Ztg.*, 1890.

[9] *Chem. News*, **85**, 255 ; *J. für Gas beleucht u. Wasservers*, 1901, p. 661.

[10] *Wied. Ann.*, **65**, 141.

[11] Madame Curie's Thesis, Faculté des Sciences de Paris (1903).

[12] *Compt. Rend.*, **122**, 420, 501, 559, 689, 762, 1086 (1896).

[13] *Proc. Roy. Soc.*, **66**, 406 (1900).

[14] *Compt. Rend.*, **127**, 175.

Soddy and Rutherford[1] demonstrated that only material carrying the β-rays was thus separated and that the so-called inactive (to the photographic plate) uranium still gave off α-rays, which ionize gases and may be detected by the electrical method. Crookes, in the same paper, reported a few preliminary experiments on thorium compounds and suggested "the possibility of separating thorium from its radioactive substance."[2]

In 1899, Debierne[3] separated from pitchblende a strong active substance which appeared to consist of titanium. On more accurate investigation,[4] however, he proved it to be nearer akin to thorium and having secured an oxide 5,000 times as active as uranium, he named the element *actinium.*

Debierne gives some four methods for separating this element, *to wit*: Precipitation of weak acid solution by sodium thiosulphate, treating the hydroxide with hydrofluoric acid and potassium fluoride, precipitation of the neutral nitrate by hydrogen dioxide and precipitating lead or barium sulphate in the liquid, whereby the active body is carried down. While quantitative physical data, as atomic weight, specific gravity, spectrum, etc., are as yet not to be had, the qualitative conduct of the radioactive properties are fairly well defined.

Hofmann and Zerban[5] examined a number of minerals from which thorium is obtained and proved the presence therein of uranium. The thorium oxides from all of these were radioactive. Norwegian gadolinite, orthite and yttrotitanite free from uranium gave a thorium oxide which neither affected the electroscope nor the photographic plate.[6] The radioactivity of actinium consists primarily of rays or "emanations," simultaneously discovered by Rutherford[7] and the Curies[8] in 1899. The gases emitted by radium and thorium are temporarily radioactive, and may be condensed at —150° and —120°, respectively.

The work of Hofmann and Zerban touching the primary activity of thorium being questioned by Barker,[9] is upheld by the

[1] *Proc. Chem. Soc.*, **18**, 121.
[2] *Loc. cit.*
[3] *Compt. Rend.*, **129**, 593.
[4] *Ibid.*, **130**, 906 (1900).
[5] *Ber. d. chem. Ges.*, **35**, 531 (1902).
[6] *Ibid.*, **35**, 533 and 145 (1902).
[7] *Phil. Mag.*, **49**, 2 (1900) ; [VI], **5**, 95 (1903).
[8] *Rapports an Congres Intern. de Physique*, **3**, 79 (1900).
[9] "Radioactivity of Thorium Minerals," *Am. J. Sci.*, **16**, 164 (1903).

junior author,[1] who determined the presence of from 0.038 to 0.04 per cent. of uranous oxide in monazite from Bahia and South Carolina. While the uranium obtained from this sand was quite radioactive, the thorium oxide discharged the electroscope in two minutes and forty seconds, two minutes and forty-five seconds, and three minutes and five seconds (the instrument without radioactive substance, three minutes and twenty-five seconds), and the β-activity affected the photographic plate in twenty-four hours. The reasons for this somewhat detailed account will shortly become apparent.

Brauner[2] reported that the heptahydrated thorium tetrammonium oxalate, which he has used in his excellent method[3] for determining the atomic weight of that element, hydrolyzed on diluting its water solution. By this means he obtained two constituents, which he designated thorium α and thorium β and ascribed the atomic weights 220 and 260-280, respectively. No subsequent publication on the subject has come from the Prague laboratory so far. At the same time the writer[4] independently reported the results of his observations, extending over some five years, which pointed toward the existence of a new element associated with thorium and gave it the name *Carolinium*. Since that time I have reported, in fragments, a number of observations in abstract along the same line. They and others are digested in this communication.

While it is unnecessary to recapitulate my first work in the leading paper referred to, it was stated that carolinium was found to be more radioactive than the original thorium. The statement was true for the body in the degree of purity had at that time when examined by the photographic, as reported, and later verified by the electrical method.[5] On page 761[6] it was stated "I am not yet ready to assert that the new substance obtained is not the third radioactive body reported by Debierne in pitchblende, actinium, which he states belongs to the iron group." From what follows it is apparent that carolinium and actinium cannot be the same. In fact, the former has little to do with radioactivity, which is the *raison d'etre* for the latter.

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[1] Zerban: *Ber. d. chem. Ges.*, **36**, 3911 (1903).

[2] *Proc. Chem. Soc.*, **17**, 67 (1901).

[3] *J. Chem. Soc.* (London), (Trans.), **73**, 951 (1898).

[4] This Journal, **23**, 761.

[5] This was kindly determined by Dr. Geo. B. Pegram, of the Physics Department of Columbia University.

[6] *Loc. cit.*

The elegant researches of Rutherford and Soddy[1] proved that there can be no doubt of the existence of a novel highly radioactive substance with thorium (thorium X), as it is usually extracted from minerals without consideration of their chemical composition, to which Hofmann and Zerban strenuously direct attention. Such prepared so-called pure salts of thorium contain a radioactive constituent, which may be concentrated chemically by precipitation with ammonia (the filtrate carries thorium X)[2] and washing the oxide with acid or even water. The residues obtained by evaporation of the ammoniacal solution in the first case are a thousand times as active as the original and "are free from thorium, or, at most, contain only the merest traces, and when redissolved in nitric acid do not appear to give any characteristic reaction" (page 376). Again the residue from the water washings became 1,800 times as active, and after conversion into sulphate, Rutherford and Soddy state, "*No other substance than thorium could be detected by chemical analysis*,[3] although, of course, the quantity was too small for a minute examination."

Having this in mind, the writer requested Dr. H. S. Miner, chemist to the Welsbach Lighting Company, to save certain ammoniacal washings obtained in the process for the extraction and purification of thorium oxide from monazite sand for the manufacture of the Welsbach gas mantles. The ignited residue, obtained from evaporating over 100 liters of this liquor, produced a marked effect upon the photographic plate and showed nearly three times the radioactivity of thorium by the electrical method, using the apparatus of Dolezalek. The radioactivity remained constant through a number of months. The body gave *none of the chemical reactions* and *did not show a single line of thorium in the arc spectrum*, made with a large Rowland grating.[4] Dr. Miner is securing an abundance of this material for us and, as soon as practicable, this will be thoroughly investigated in our laboratory.

The writer, working with Lichtenthaeler,[5] has obtained highly radioactive bodies, tested by the photographic method, from thorium, cerium, didymium oxides and the residual phosphates, ex-

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[1] *Proc. Chem. Soc.* (London), **18**, 2 (1902).

[2] Rutherford and Soddy : *Phil. Mag.*, 1902, p. 370.

[3] Italics theirs.

[4] By Dr. W. J. Humphreys of the Broadway Rouss Physical Laboratory, University of Virginia.

[5] Thesis for degree of Master of Science, unpublished.

tracted by ourselves from North Carolina monazite sands. Further, we obtained an extremely active body by precipitating the sulphate solution with hydrogen sulphide, which perhaps would, but not necessarily, indicate the presence of polonium,[1] according to the Curies.

When we consider that barium chloride containing radium may be precipitated by sulphuric acid or silver nitrate and the filtrate or precipitate obtained thereby, supposedly containing none of that remarkable body, is still radioactive,[2] we can easily understand how in a mineral or salt a radioactive body, perhaps resembling one of the constituents, clings to various components throughout many chemical manipulations. It having been suggested that uranium might owe its radioactive properties to the presence of small amounts of polonium or radium, Mme. Curie[3] states that such could not be true and adds in another paper[4] "the property of emitting rays..................which act on photographic plates is a *specific property of uranium and thorium.*" "The physical condition of the metal seems to be of an altogether secondary importance." "Uranium and thorium alone are practically active."

It is very foreign from the intention of the writer to be hypercritical of work which stands out so brilliantly and will remain so for a long time to come, but very painstaking investigations have caused him to face about in this matter, not an unusual condition for scientific truth-seekers. The power possessed by the thorium, as usually prepared, of inducing activity, reported by Rutherford and his co-workers,[5] is deeply interesting and supports our thesis. The brilliant French woman states concerning uranium:[6] "I have never found any marked difference between the relative activities of the same compounds." By analogy one may consistently assume the same for thorium. We have obtained similar compounds of thorium fractions which do differ in their radioactivity, in some cases one being three times as great.

Metzger[7] has published an interesting and novel method for separating thorium from cerium, lanthanum and the didymium

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[1] *Compt. Rend.*, **127**, 175 (1898).

[2] See the works of the Curies, Geisel, Elster, and Geitel, Markwald, and others.

[3] *Revue générale des Sciences*, January, 1899; M. and Mme. Curie: *Compt. Rend.*, **127**, 175.

[4] M. and Mme Curie and M. Bémont: *Compt. Rend.*, **127**, 1215.

[5] *Loc. cit.*

[6] *Ibid.*

[7] This Journal, **24**, 901.

depending upon its precipitation from a neutral solution by a 40 per cent. alcoholic solution of fumaric acid. The writer and Lemly[1] have verified these observations as far as ordinary analytical methods are concerned. Applying it to the accepted chemically pure thorium, however, we obtained a filtrate less than 0.5 per cent., which, on evaporation and ignition, gave a grayish oxide possessing such marked radioactivity by the electrical method that Dr. Pegram stated it acted as if "salted with radium."[2] This decayed very rapidly from 42 to 12.4 in eight days, to 3.3 in nine days more (uranium being taken as standard at unity). After thirty-two days more it gave 3 and was practically constant. The corresponding values obtained for the thorium precipitate, which constituted virtually the whole, were 0.63, 0.92 and 1. Truly but one interpretation of these results may logically be had, namely, the existence of a radioactive body with thorium, which is different from it. Crookes has sounded a timely warning against depending upon the photographic method for determining the radioactivity, so we have been guided mainly by the electrical method. Yet most interesting observations may be had by the photographic method, which has been used to secure very rough quantitative results, but by no means comparable to the other procedure. It aids one much in learning the β-activity, whereas the α-rays are the most important factor in the ionization of gases upon which depends the electrical method. Persistent differences in radioactivity of the preparations had by different chemical methods, have been noted and the same method of preparation has given persistent differences in radioactivity measured by the same and different methods.

Rutherford[3] and the Curies[4] have shown that the α-radiations, or "emanations," according to the former, as adverted to, are readily driven away from radium halides and thorium oxide and condensed by liquid air. It does not come within the scope of this paper to discuss the nature of these emanations, which will be dealt with by the author and Lockhart[5] in another communication. Suffice it to say that we have repeated this work success-

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[1] Unpublished work.

[2] Personal correspondence. In time Dr. Pegram will no doubt publish a full discussion of all the results.

[3] *Loc. cit.*

[4] *Ibid.*

[5] Soon to be published.

fully and we have applied the same test to a large number of authenticated radioactive minerals, and in every case where those minerals have been known to contain helium we have succeeded in condensing the emanations from them. We have obtained the emanations from uranium- and thorium-bearing minerals, and we have failed to secure emanations condensed on a fluorescent zinc sulphide screen from minerals containing thorium.

The extremely interesting work by Rutherford, with his able associate Soddy and their students, on the regeneration of thorium X, at first thought would apparently convince one that thorium is primarily radioactive, but this can be explained by the presence of minute amounts of a foreign highly active substance, which so far has failed to be sufficiently concentrated for a thorough chemical examination, and yet exercises continually the novel property of inducing radioactivity. It is not hazardous to venture the opinion that it will prove to be actinium. In the light of the facts enumerated, however, it appears that thorium is not primarily a radioactive body any more than water containing a radium salt is primarily radioactive, because the radioactivity appears therein after it is distilled. It must be distinctly understood that no criticism is being passed upon the brilliant investigations progressing so successfully in the McGill laboratory on this extraordinary phenomenon of radioactivity, whatever be its source. It must be remembered that radioactivity is far more delicate than the spectroscope: consequently a notable per cent. of a body possessing that property may be present before any spectroscopic evidence may be had, as noted in Demarçay's work on radium. Further, the compounds of this element exhibit unusual radioactive strength before any change whatever is measurable in the atomic weight of the barium with which it is associated.

Although we have not as yet secured a thorium preparation free from any radioactivity, our observations confirm those of Rutherford and his co-laborers. The conclusion thus arrived at is that thorium, as ordinarily extracted from mixed or complex minerals, contains a primary radioactive body, perhaps similar to the truer thorium, but not necessarily so.

From what has been said, that which follows may be considered as if there were no such thing as radioactivity, as the amount of the body possessing that property is entirely negligible from a spectroscopic standpoint and far too small to produce the marked physical and chemical changes in pure thorium now to be briefly recounted.

Some years ago the writer and Davis began work on the atomic weight of thorium. A full account of the objections to the former methods will be given in due time. Working with materials from various sources, such variable results were obtained that they could not be attributed to faulty methods. In the light of the research of Brauner and the observations made in this laboratory, the problem resolved itself into securing a pure substance, as free from its contaminating constituents as possible.

In the work of Jefferson and Smith[1] on the separation of the rare earths by means of organic bases, it was stated that thorium gives a yellow precipitate with phenyl hydrazine. Allen[2] remarks that with pure thorium and pure phenyl hydrazine the precipitate is white and quantitative. Although Allen does not state that the source of this material was free from uranium, it may be that both of these observations are correct, as noted previously by the author and Lemly.[3] The precipitate, produced by phenyl hydrazine with very pure thorium, is at first white and gelatinous, but soon acquires color, doubtless due to decomposition of the precipitant. We have observed that fractionation of thorium can be brought about by means of phenyl hydrazine. By addition of an insufficient amount of the reagent one obtains first a heavy flocculent precipitate, which soon acquires color. On addition of more of the reagent there is obtained a gelatinous, white precipitate, which also acquires color as the precipitant decomposes. These substances are different, as shown by variations in the radioactivity, determined by both methods and the solubility of the oxides in hydrochloric acid.

So far we have found it impracticable to fraction thorium compounds on a large laboratory scale with phenyl hydrazine. The gelatinous precipitate clogs up the filtering media we have tried. Upward suction through unglazed porcelain, which has served so satisfactorily in much of the work on the rare earths in this laboratory, failed utterly.

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[1] "Aromatic Bases as Precipitants for Rare Earth Metals," this Journal, **24**, 540 (1902).

[2] This Journal, **25**, 421.

[3] Unpublished work. Reported in abstract at the Pittsburg meeting of the American Chemical Society, 1902.

Attention must be directed to the fact that all the different constituents are precipitated by this reagent, but at different rates; hence the speed of the reactions was the point of attack. The difficulty was not one of simple filtration, which may be carried out readily enough after the precipitates have formed and settled, but of rapid separation, thus avoiding a second formidable hindrance, namely, decomposition of the phenyl hydrazine with corresponding variations in the reactions. The use of a centrifuge offered promise. It was successful, and perhaps may be used on a commercial scale, although for reasons which follow it is not recommended. With the machine at our disposal we could work with but 20 cc. at a time. The solution must be weak and a small batch amounted to 10 liters. We regarded it essential that sufficient material be prepared for further purification and investigation, an ample supply being at hand through the generosity of the Welsbach Lighting Company. The writer did not feel that he had more time than the average allotment of life to a chemist, thirty years, so attempted a rough-and-ready settling and decantation with one lot of 10 liters, but with poor success. The old fractional precipitation of the rare earths by ammonia, complained of by Crookes, Hood and others, is mere child's play in comparison with the time-robbing and indefinite fractionation by this aromatic base. A separation of thorium into different constituents was brought about, as shown by atomic weight determinations of different portions. Fractions were had (as tetrad) giving 214, 228, 235, 242, 249 and 252, the original giving 232.5 and 232.6.

This procedure was temporarily abandoned to make use of the method earlier pursued in fractionation and later in the efforts of Dr. Davis and myself to determine the atomic weight of thorium, namely, preparation of the pure crystalline tetrachloride by heating pure thorium dioxide mixed with pure sugar carbon in an atmosphere of chlorine. It is unnecessary, in this paper, to give the details of our procedure, which will be described later in full, further than to say we found it unadvisable to use hard combustion glass tubing as variable amounts of contaminating chlorides were formed from the glass. We found we could not settle upon a definite correction for these impurities, as did Richards[1] in his elegant work on uranium.

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[1] "Atomic Weight of Uranium," Richards and Merigold, *Chem. News*, **85**, 177, 186, 201, 207, 222, 229, 249 (1902).

Quartz tubes, 2 cm. in diameter, made to order, were placed within large porcelain tubes, which rested in a powerful combustion furnace. A carbon boat containing the mixture of thorium oxide and carbon was inserted in the end of the quartz tube. Pure chlorine, free from oxygen, was carefully dried as it issued from a cylinder by elaborate desiccating apparatus and led in by means of a smaller quartz tube so that the stream of gas played directly into the boat. Arrangements were made by glass cocks to prevent a back flow of any volatile body that might be produced.

As previously noted, by Berzelius and the author, when this method is followed out, there is obtained a volatile chloride. "weisser dampff," absorbable by alcohol, which, according to the former, is *not* thorium, yet comes from pure compounds of that element. This has been verified by applying the method to thorium obtained from a number of sources, including a small amount of a very pure preparation used by Cleve in his atomic weight determinations and presented to Dr. F. W. Clarke, of Washington, who kindly loaned the preparation to us. It, therefore, appears that the volatile chloride is to be had from thorium itself, or that material which separates with thorium in its extraction from various minerals.

Beautiful fern-like crystals of thorium tetrachloride formed on the inner walls of the quartz tubes. There remained in the carbon boat variable amounts of residue, largely converted into chloride, depending upon the temperature of the furnace and duration of the heating, from two to ten hours. These accumulated residues were converted into the oxide and subjected to similar treatment several times. With each repetition there were diminishing amounts of the volatile chloride and sublimed thorium tetrachloride formed. After the third redistillation the oxide from the residue was digested in hydrofluoric acid and concentrated hydrochloric acid to remove accumulated impurities from the carbon and quartz tube. This oxide is *soluble in concentrated hydrochloric acid*, from which it may be crystallized by evaporation. This is not the novel thorium oxide, Th_3O_5, described by Locke,[1] or that unique compound of thorium which has caused the spirited controversy between Stevens[2] and Wyrouboff and Verneuil.[3] The material thus obtained gave an atomic weight of 241.7 (tetrad).

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[1] *Ztschr. anorg. Chem.*, **7**, 345 (1894).

[2] *Ibid.*, **27**, 41 (1901) ; **31**, 368 (1902).

[3] *Ibid.*, **28**, 90 (1901) ; **32**, 376 (1902).

This chloride was recrystallized from concentrated hydrochloric acid, three times, until the fine, white needle-crystals appeared the same. The material was converted into the oxide, by solution in water, in which it was readily soluble, giving a perfectly clear solution, absolutely devoid of any opalescence,[1] precipitation by ammonia, and igniting the washed white gelatinous hydroxide in platinum. It was digested in turn with dilute hydrochloric, nitric and hydrofluoric acids, washed with pure water and brought to a constant weight.

In our first published work on thorium some store was laid by the specific gravities of the oxides of the several fractions as a means for watching the course of the disintegration. Some doubt was thrown upon this method of control through work of the writer and Mills,[2] as variations in the value of the same preparations were had depending upon the method employed. It was learned, however, that satisfactory comparable figures were obtained when the oxide was prepared in the same way each time.

The specific gravity of this oxide was determined:

Amount taken. Gram.	Specific gravity.
0.7992	11.25
0.8973	11.27

The specific gravity of the original pure thorium oxide:[3]

Amount taken. Grams.	Specific gravity.
2.0730	10.54
3.4573	10.51

The atomic weight was then determined:[4]

Oxide used.	Sulphate obtained.	Equivalent.	Atomic weight.
1.559290	2.434914	63.875	255.5
0.524254	0.819365	63.975	255.9
0.549331	0.854810	63.900	255.6

The familiar method used was essentially that of G. Krüss with certain variations, namely, a specially devised platinum-lined, asbestos jacketed bath was used and the temperature judged by

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[1] See Locke's chloride.

[2] Unpublished.

[3] This work was done by the writer and S. Jordan and will later be published in full.

[4] Unpublished by the author and R. O. E. Davis.

a thermometer in which mercury was under a pressure of twenty atmospheres, capable of registering 560° C. It was standardized by the Reichs-Anstalt.

It is scarcely the time or place to discuss the sulphate method, which will be dealt with fully later. It is well known[1] that the method does not possess the most desirable degree of accuracy, but it answers entirely for such work as is here reported. The treatment with new amounts of sulphuric acid was continued until constant weights were had. It is, perhaps, just as well to state that the weights used were gold-plated and corrected by the Bureau of Standards in Washington; the vibration method was used with a highly sensitive Sartorius balance[2] resting upon a brick-cement pillar and that the pans were so loaded each time with counterpoises and standardized platinized weights as to bring the apparatus to a determined point of the highest sensitiveness. Further, it may not be out of place to state at this point that after removal from the porcelain tube the material used did not come in contact with anything other than Jena glass and platinum; that the water, acids and ammonia used were redistilled in platinum and gave no weighable residues after evaporation. The sulphuric acid was not redistilled, but the very fine product, especially secured, gave no residue on evaporation of 50 cc., and if it had, it would have tended to lower the atomic mass value.

It is here quite interesting to note that Hofmann and Zerban[3] state that the equivalent of "actinium" has been found to be 63.32 or 253.28 atomic weight, whereas that for pure thorium is 58.1, or 232.4 ($O = 16$). Carolinium oxide shows a radioactivity of 0.56 and 0.6 (original thorium oxide $= 1$) by the electrical method. The two values were obtained from the same material after an interval of six weeks. Our preparation on heating almost to white heat gave off no "emanation" condensable by liquid air upon a zinc sulphide screen.

The volatile chloride was collected, in part, by its absorption in alcohol and condensation as acicular crystals in the cooler portions of the porcelain tubes. These were dissolved in water and the whole evaporated to dryness, the oxide digested by turn in hydrofluoric, concentrated hydrochloric and nitric acids, and then

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[1] "Rare Earth Crusade," *Science*, N. S.

[2] Constructed for Dr. F. P. Venable; see his work on zirconium, this Journal.

[3] *Ber. d. chem. Ges.*, **36**, 3093 (1903).

dissolved in hot sulphuric acid (1 : 1), the gelatinous white hydroxide precipitated by ammonia, washed, and ignited to a constant weight in platinum.[1]

The specific gravity of this oxide was determined:

Amount taken. Grams.	Specific gravity.[2]
1.9207	8.442
1.8465	8.512

The atomic weight obtained, assuming its tetravalence:

Oxide used.	Sulphate found.	Equivalent.	Atomic weight.
0.306778	0.505705	53.375	213.5
0.320618	0.530890	53.000	212.0
0.794692	1.309245	53.175	212.7

It is very interesting to note that the oxide obtained from this volatile chloride possesses very slight radioactivity, about one-third that of the original thorium, when tested by the electrical method. An exposure to a sensitive photographic plate for seventy-two hours showed that it possesses radioactivity which affects the photographic plate to a very limited degree. It does not give off emanations condensed at the temperature of liquid air, as judged by the effect on a phosphorescent zinc sulphide screen.

Although we know that this material is not yet pure, for reasons which will be given in the following, the novel properties mentioned above and its contrasting chemical conduct enumerated below warrant the statement that we have a new element. Berzelius was the first to observe the formation of this "weisser dampff." On account of his beautiful pioneer researches in the difficult field, as the discoverer of thorium from which it comes, it is only proper that it should bear his name, so I have designated the element *berzelium*, with the symbol Bz.

Just a few words concerning the new thorium, or thorium freed, in a measure, from carolinium and berzelium, are called for here, as that element will be treated of more fully in a later communication. In our former paper[3] the values obtained for the atomic weight of thorium from the tetrachloride were 222-223.3. It was

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[1] I have been assisted in this part of the work by P. Irwin.

[2] On page 766, in my former paper (*Loc. cit.*), small amounts of oxides were obtained giving specific gravities 8.77, 8.47, and 11.26.

[3] *Loc. cit.*, p. 771.

distinctly stated that the values were preliminary and are not to be taken as final on account of the small amount of material used in each determination. More material has been secured, purified by treatment with acids, as mentioned above, and atomic weight determinations made according to the sulphate method.

Following are the values found:

Oxide used.	Sulphate found.	Equivalent.	Atomic weight.
0.425456	0.694934	55.15	220.6
0.740052	1.210405	55.025	220.1

Doubtless Chroustchoff's russium and Brauner's thorium α were quite pure preparations of thorium.

The source of heat for our furnace was gasoline gas, which does not have a constant pressure, consequently there can be no question, but there is present in this middle portion variable, but small, amounts of carolinium and berzelium, and that some thorium is in the two extremes. We have just received a specially constructed electric oven from Heraeus and a Le Chatelier pyrometer. so that the process may be controlled with precision. This apparatus has been purchased through a grant from the Carnegie Institution, received this year.

Although these constituents are not yet in the most desirable and highest state of purity, it became important to learn their comparative conduct under certain influences, physical and chemical.

It may be recalled that Kunz[1] and the author examined the action of ultraviolet light, Roentgen rays, cathode rays, and the complex radiations and emanations of radium rays upon a large number of gems and minerals in the Morgan-Tiffany and Morgan-Bement collections of the American Museum of Natural History in New York. At that time the writer[2] also observed the action on many of the rare earth oxides of ultraviolet light produced by sparking high voltage currents between iron terminals. The dioxides of zirconium and thorium only became phosphorescent under such stimulation. One is radioactive, the other not. Uranium oxide, which is radioactive, did not respond. The new thorium oxide phosphoresced beautifully white on a five-minute exposure, while berzelium and carolinium oxides gave negative results. Carolinium oxide, containing variable amounts of tho-

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[1] *Science*, N. S., **18**, 769 (1903).

[2] *Chem. News*, **88**, 262; *Am. J. Sci.* **16**, 465 (1903).

rium, responded in proportion to the latter constituent present. We believe this is perhaps the first application of the method to the examination of material in the course of chemical investigations, as suggested by Kunz and Baskerville.

We have learned that ordinarily accepted pure crystalline thorium chloride, when thrown upon a filter-paper from concentrated hydrochloric acid, may be washed with water, a clear solution resulting. Berzelium and carolinium chlorides act similarly. When thorium is freed from these, the body will remain upon the filter-paper and may be washed with concentrated hydrochloric acid, but as soon as pure water is added, it hydrolyzes and gives a turbid filtrate, acting in exactly the same way that titanium does. This was not suspected, although, after the observation was made (by Jordan in this laboratory), it is no more than one might expect. As zirconium does not act like titanium, the natural inference is that it contains some hindering element, perhaps the earth, reported by Hofmann and Prandtl in zirconium from euxenite.[1]

The hydroxides of these three substances are white and gelatinous, insoluble in ammonium, sodium or potassium hydroxide, readily soluble in the ordinary acids. Carolinium oxide is grayish with pink tinge, thorium, white with merest tendency toward green, and berzelium has a more marked leaning towards green. These remarks are applicable to the substances in that state of purity so far had. The oxides of thorium and berzelium are not soluble in hot, concentrated hydrochloric acid even when the digestion has lasted three weeks. Carolinium oxide dissolves slowly but completely, within a few days and the chloride forms fine crystals on concentration of the solution, quite different from ordinary thorium chloride. All three are readily precipitated by the ordinary thorium reagents, *viz.*, ammonium oxalate, sodium thiosulphate, hydrogen dioxide, potassium periodate, etc. Their salts behave differently with various organic bases. Phenyl hydrazine, after a time in the cold, gives a precipitate which becomes yellow, berzelium red and thorium orange. Pyridine precipitates thorium at once, carolinium slowly and berzelium with extreme slowness and incompletely. Xylidine precipitates both the former, but not berzelium. o-Toluidine gives a pinkish precipitate with thorium, a white flocculent one with carolinium and none with berzelium. Thorium is completely precipitated by fumaric acid.

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[1] *Ber. d. chem. Ges.*, **34**, 1064 (1901).

carolinium only partially, a clear filtrate being had in both cases. Berzelium is precipitated nearly completely by fumaric acid; the filtrate is rendered opalescent by ammonia, however.

The solutions of none of these gave absorption bands. Dr. W. J. Humphreys, of the Rouss Physical Laboratory, University of Virginia, kindly examined the arc spectra with a Rowland grating, 21 feet in diameter and 20,000 lines to the inch. His examination, covering the region between 3,900 and 5,500, showed some differences between berzelium and the other two, but his conclusion was that the differences in the spectra, or those portions of the three materials which give arc spectra, might be accounted for by impurities, or, at any rate, were not sufficient to warrant the statement from his spectral data that they are not the same.

Small portions of the impure materials have been sent to Sir William Crookes, by request, to be examined in the ultraviolet region with the apparatus used in his beautiful mapping of the spectrum of radium.

SUMMARY.

(1) The preponderance of evidence indicates that thorium is not a primary radioactive body.

(2) There can be no question from the work of Chroustschoff, Brauner, Crookes, Rutherford, Auer, and the author but thorium is complex and not a chemical element, as we accept the term.

(3) From the experimental data, physical and chemical, outlined in this communication, it appears that thorium has been resolved into at least three simpler substances and that they are sufficiently identified to deserve distinct names.

(4) The conservative position, in which the author coincides, concerning the acceptance of novel members of the family of elements, is the requirement of spark spectral confirmation. At the same time it must be kept in mind that even spectral work requires unification.[1]

(5) As stated above, one of the objects of this paper is to present work to guide others and seek confirmation in other hands. While we shall be busied with the investigation, instead of asking a reservation, we would invite others to assist in solving the problem.

UNIVERSITY OF NORTH CAROLINA,
April, 1904.

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[1] See my address before Section C., A. A. A. S., St. Louis meeting, December, 1903.

ADDENDUM.

Since the paper was written and presented, a letter from Sir William Crookes has been received, excerpts from which are given herewith. "I had not quite sufficient to enable me to photograph the whole ultraviolet spectrum, but I have taken that portion, between wave-lengths 3444.020 and 4071.903. which contain some very characteristic thorium lines. I compared the spectra with my standard thorium spectrum taken from the spark between the poles of metallic thorium. Making allowance for the fact that my spectrum is from the metal, while that from your material is from the chloride solutions, all five spectra are practically identical, all the prominent lines being seen in each spectrum, while there are no lines in one which are not seen in the others................ You must not attach too great importance to these spectrum results. All I can say is that they give no positive proof of the existence of anything new. But they by no means prove that such bodies do not exist. They may be there with their spectra, masked by the thorium, which is present."

As only a limited portion of the spectrum was examined, the question is still an open one. My sincere thanks are due Sir William Crookes.

June 18, 1904.

RUTHENIUM, VI: THE BROMIDES.

By Jas. Lewis Howe.

Received June 24, 1904.

In order to determine whether the bromides of ruthenium correspond to the chlorides, several members of the different series have been prepared and are described in this paper. It was found that the salts of the bromruthenite, X'_2RuBr_5, 'aquo'-bromruthenate, $X'_2Ru(H_2O)Br_5$, and bromruthenate, X'_2RuBr_6, series differ very slightly from the corresponding chlorides, but are rather more soluble and more easily decomposed. This has rendered their preparation, and especially their purification, more difficult, so that sufficient time only has been put upon them to learn their general character.

The bromruthenous acid was prepared by the action of hydrobromic acid upon ruthenium tetroxide, RuO_4. On covering the