Discovery of actinium and the thorium isotope ^{230}Th

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Introduction

The history of the discovery of actinium is described in the context of the definition of chemical elements. This element was discovered by Friedrich Giesel[1] in 1902 who had named it first emanium. In 1900 Andre Debierne[2] looking for a new radioactive element in pitchblende had found in an ammonia precipitation a substance with high radioactivity which was chemically similar to thorium and named it actinium. He really had discovered one of the first chemically inseparable radioactive elements, which were later identified as isotopes. Because it was not a new element for him, he took over the discovery of Giesel, and explained in 1904 that Giesel´s emanium was identical with his thorium-like actinium. Some details about the discovery of actinium are written in a paper in German,[3] and in this paper is given an explaination why Debierne had rejected his own discovery and took over the discovery of Giesel.

The discovery of a new radioactive substance by Debierne

After Pierre and Marie Curie had discovered polonium and radium they proposed their co-worker André Debierne to look for other undiscovered radioactive elements in pitchblende. In 1899 Debierne had investigated the residue of uranium minerals from which the uranium had been removed in a mill. After removing of the known radioactive elements polonium and radium he added ammonia to the acidic solution and obtained a precipitation mainly consisting of the hydroxides of aluminium and iron which showed low radioactivity. From this he isolated titanium and found that the radioactivity of the preparation with analytical qualities of titanium was more than hundred thousand fold stronger than uranium and was neither originated from radium nor from polonium. He named this new element actinium. [4] In his paper he didn´t describe in detail the chemical procedure.

In 1900 he wrote that he has continued his work about this radioactive substance, and explained that it had more similarity with thorium. He repeated that he had discovered a new

[1] Friedrich Oskar Giesel (1852-1927) was a German chemist. During his work in the chemical factory of Buchler & Company´s chemical factory in Brunswick, Germany, he started with the organic chemistry and after the discovery of radioactivity he has done research on radioactive elements.
[2] Andre-Louis Debierne (1874-1949) studied physis and chemistry and was working as assistant of Pierre Curie and after its death he helped Marie Curie in preparation of radium salts.
[3] Niese S.: Die Entdeckung des Actiniums. Mitteilungen der Fachgruppe Geschichte der Chemie der Gesellschaft Deutscher Chemiker. 23, 129-144 (2013)
[4] Debierne A.- L.: Sur un nouvelle matière. Comptes rendus heptomadaires des sciences de l´ Académie des sciences (Abbr. C. r.). 129, 593-595 (1899)

radioactive element, because known compounds of thorium are of lower radioactivity. [5] Really he had measured the radioactivity of thorium isotopes. The description of chemical procedures are not clear. Therefore it was not possible to repeat his procedures. He also never had given the preparations described in his publications 1899 and 1900 to any other scientist. He didn´t believe that the measured radioactivity came from another kind of thorium. Therefore he had written that in future he will isolate the new element being the carrier of high radioactivity in his substance.

Friedrich Giesel discovered emanium, a new element which was similar with lanthanum

Friedrich Giesel was fascinated, when his friends the teachers at the gymnasium in Wolfenbüttel Julius Elster and Hans Geitel had informed him about the discovery of polonium in pitchblende by Marie and Pierre Curie shortly after their publication.[6] He immediately ordered uranium minerals and residues from the production of uranium pigments from the chemical factory de Haen in List near Hannover and started with the separation of polonium and radium. Looking for the separation of polonium he found in the sulfuric acid solution of uranium minerals a barium containing residue which was highly radioactive.[7] Before he had investigated this precipitation in detail M. and P. Curie published the discovery of radium. Then Giesel studied the crystallization of barium salts and found that radium could be enriched faster with bromides than with chlorides. In 1902 a special department of the factory was founded to produce radium. This enabled him to supply other researchers e.g. Rutherford in Montreal, Stefan Meyer in Vienna and even Marie and Pierre Curie with radium. Giesel had determined the deviation of the radiation in a magnetic field, and the flame spectra of radium, which colored the flame of a Bunsen burner in a beautifully carmine red.[8] In 1900 when he had produced 2kg radium-barium bromide he obtained by addition of ammonia to the mother liquor from the re-crystallization of the bromides a radioactive precipitate. After its dissolution he isolated a small amount of radioactive rare earth with oxalate.[9] In 1902 he precipitated with oxalate radioactive rare earth together with lanthanum and obtained a substance which intensively released emanation and found an enrichment of an active substance by fractionated crystallization of oxalates from diluted nitric acid. In the obtained substance the thorium content was very low. In this paper he first described the use

[5] Debierne A.- L.: Sur un nouvelle matière radio-actif l'actinium. C. r. 130, 906–908 (1900)
[6] Curie P, Curie M, Sur une substance nouvelle radio-active, contenue dans la pechblende, C. r. 127, 175-178 (1898)
[7] Giesel F.: Einiges über das Verhalten von radioactiven Baryt und über Polonium. Ann. Phys. 69, 91-94 ; Über Radium und Polonium. Physik. Z. 1, 16-19 (1899)
[8] Giesel F.: Ueber radioactives Baryum und Polonium. Ber. Dtsch. Chem. Ges. 33, 1665-1668 (1900)
[9] Giesel F.: Über radioactive Stoffe. Ber. Dtsch. Chem. Ges. 33, 3569-3571 (1900)

of fractionated crystallization of oxalates to separate radioactive rare earths from thorium.[10] The spark spectrum of his preparation shows only lanthanum and a small amount of cerium but no thorium or barium.[11] In 1904 Giesel was sure to have discovered a new element, described its similarity with lanthanum and named it „emanium".[12] He explained it as companion of lanthanum, and had no doubt that this substance was a new element, different from radium.[13] The radioactivity of its solid salts reached a constant maximum about one month after precipitation because he not had measured the low energy beta rays of his discovered emanium (^{227}Ac) but the alpha rays of the daughter nuclides ^{227}Th and ^{223} Ra. The behavior of decay, the co-precipitation with lanthanum, and its purification are reasons to accept that his emanium was ^{227}Ac.

Debierne takes over the discovery of Giesel and was accepted as discoverer of the element 87

In the paper published in 1899 Debierne started with a statement that polonium and radium were new chemical elements and explained that Marie and Piere Curie had proposed him to look for further new radioactive elements in pitchblende. Debierne was certain that emanium discoverd by Giesel really was a new chemical element. Therefore he explained that the actinium, discovered by him in 1899 was identical with the emanium of Giesel. He repeated the procedures published by Giesel in 1904 and wrote that his discovered actinium could be also co-precipitated with lanthanum and explained that he but not Giesel had discovered the new element.[14] Giesel has been astonished about Debierne´s new paper, in which was written that his emanium should be identical with Debierne´s actinium. Debierne had not answered on publications and letters from Giesel. Even when Giesel had sent a sample of his emanium to Marie and Pierre Curie he obtained no answer. Then Giesel travelled to Paris but there he got no answer to his questions.[15] Debierne however became very active. In a session of the Parisian Academia of Sciences he explained again, that Giesel´s emanium is identical with his actinium, described in 1889 and pronounced that he had tried unsuccessfully to contact Giesel. This lecture appeared soon in a German translation in the „Physikalische Zeitschrift",[16] but not in "Berichte der Deutschen Chemischen Gesellschaft" where Giesel had published all his experiments with emanium.

[10] Giesel F.: Über Radium und radioactive Stoffe. Ber. Dtsch. Chem. Ges. 35, 3608–3611 (1902)
[11] Runge C., Precht J.: Über das Funkenspektrum des Radiums. Ann. Physik 317, 407-412 (1903)
[12] Giesel F.: Über den Emanationskörper aus Pechblende und über Radium. Ber. Dtsch. Chem. Ges. 36, 342-347 (1903)
[13] Giesel F.: Über den Emanationskörper (Emanium). Ber. Dtsch. Chem. Ges. 37, 1996 (1904)
[14] Debierne A.- L.: Sur l´actinium. C. r. 139, 538-540 (1904)
[15] Fricke R. G. A.: Friedrich Oskar Giesel – Pionier der Radioaktivitätsforschung. Opfer seiner Wissenschaft, AF-Verlag, Wolfenbüttel (2001)
[16] Debierne A.- L.: Über das Aktinium. Physik. Z. 5, 732-34 (1904)

Because of Debierne´s false statement, Giesel answered that only he had given the opportunity for a comparison when he visited Paris and had handed over emanium samples to other scientists. He wrote that Mr. Debierne had not replied to his publications, which appeared within three years, although he pointed-out a possible identity with actinium. Debierne had not fulfilled his desire to give a small sample of his preparation for comparison nevertheless Giesel had delivered Miss Curie a sample of his preparation. In Paris Giesel had not seen the old thor-actinium-samples but only the new ones. Giesel didn´t allow a curtailment of his discovery, which he had done completely independent.[17] After discussion with Giesel the Curies decided to send the new preparation of Debierne together with a preparation of Giesel to William Ramsay from university college London. He gave them to Otto Hahn and Otto Sackur who were working there at that time. They found that both substances are emanating whereby the substance from Giesel was more pure than that of Debierne.[18] Nevertheless Debierne was accepted as discoverer of actinium instead of Giesel and the name actinium, too. Hahn had never forgotten this situation. He wrote in his memoirs "that they had demonstrated by the half live of both substances, that it was the same element. For Giesel the substance was similar with lanthanum and for Debierne with thorium." [19]

The discovery of the precursor of radium by Bertran Boltwood in 1907

In 1907 the first hint that the element which was described and named actinium in 1900 by Debierne was not similar with rare earth elements but a kind of thorium came from Bertran Boltwood.[20] He was looking for an assumed long lived precursor of radium which shows in minerals a constant activity ratio with uranium. Because he could not find ^{226}Ra in purified uranium even after a long time, he concluded that uranium didn´t decay directly to radium but there must be another long-lived radioactive element between uranium and radium. At first he assumed that the missed element was actinium which Debierne had described. Boltwood purified a preparation which he had obtained according to the publication of Debierne in 1899, and in 1900 despite of lack of experimental details. After some time in his substance Boltwood found radium which was built by the decay of the thorium like preparation. Then he isolated the emanium described by Giesel in 1902 and purified it together with r. e. e. In this

[17] Giesel F.: Über Aktinium-Emanation (Erwiderung an Herrn A. Debierne). Physik. Z. 5, 822-823 (1904)
[18] Hahn O., Sackur O.: Die Zerfallskonstanten der Emanationen des Emaniums und Actiniums. Ber. Dtsch. Chem. Ges. 18, 1943-946 (1905)
[19] Hahn O.: Vom Radiothor zur Uranspaltung: eine wissenschaftliche Selbstbiographie. Vieweg, Braunschweig (1962)
[20] Kovarik A. F.: Bertram Bolden Boltwood, 1870 – 1927. National Academie of Sciences of the United Staates of America, Biographical Memoires, Vol. XIV, Third Memoir (1928)

emanium he could not find radium even after a long decay time.[21] Boltwood explained the thorium-like preparation obtained by him after the procedure described by Debierne in 1899 as a new radioactive element and named it ionium which is now known as isotope of thorium (^{230}Th). It was identical with or the main radioactive component of Debierne´s in 1899 described preparation. Since that time was evident, that Debierne had not discovered the element number 87 but had found the radioactive element, which Boltwood had named ionium and was accepted at first as a new element and later as a new isotope of thorium. In 1907 Boltwood wrote in a letter to Rutherford: „It is a curious and interesting fact that ionium was the chief, if not the only radioactive constituent of the radioactive substance that I separated from pitchblende in 1899 and which I had always supposed was actinium owing to Debierne´s perfectly rotten statements in the matter. I think that Debierne has probably had the stuff in his hands for years and has not the sense to identify it." [22]

Why Debierne had rejected his own discovery

In 1900 Debierne described that he had discovered in pitchblende a new element which he named actinium. It was similar to thorium but shows a higher radioactivity than thorium. He didn´t believe that the measured radioactivity was another kind of thorium and wrote that he had planned to separate his discovered element from thorium. His actinium named element was indeed the first radioactive substance which was similar with a known element and because of its higher radioactivity at that time it would have been accepted as a new element and later as an isotope of thorium. In the same year radioactive lead was discovered by Hofmann and Strauss which first was accepted as a new element and later identified as an isotope of lead.[23] When Otto Hahn in 1905 had discovered Radiothor, (^{228}Th) it was accepted as a new element and later as isotope of thorium, too.[24]

Debierne was looking for a new element and until his discovery there are no problems with the definition of Antoine Lavoisier of chemical elements "… by the term *elements* mean to express those simple and indivisible atoms of which matter is composed, it is extremely probable we know nothing at all about them; but, if we apply the term *elements*, or *principles of bodies*, to express our idea of the last point of which analysis capable, by any means, to reduce bodies by decomposition. Not that we are entitled to affirm, that these substances we consider as simple may not be compounded of two ore even of a greater number of

[21] Boltwood B.: On Ionium, a New Radio-Active Element. American Journal of Science 25, 365 (1908)
[22] Kirby, H. W.: The discoverer of Actinium. ISIS Chicago Journals 62, 290 – 308 (1971)
[23] Hofmann K. A., Strauss E.: Radioactives Blei und radioactive seltene Erden", Ber. Dtsch. Chem. Ges. 33, 3126-3131 (1900)
[24] Hahn O.: A new radio-active element, which evolves thorium emanation, preliminary communication, Proc. R. Soc. Lond. A 76, 115-117 (1905)

principles …". [25] While until the middle of the 19th century the elements were discovered by new chemical properties of substances in weightable amounts, later some elements were first identified spectroscopically, e. g. rubidium and caesium in mineral water in 1861. In a similar way Marie and Pierre Curie discovered first polonium and then radium by radiation which ionize air. [26] They identified some chemical properties and in the case of radium later they isolated weighable amounts. These new radioactive elements were not in contrast to Lavoisier´s definition of chemical elements.

The year 1900 is characterized by preluding the research about radioactive isotopes. New radioactive substances had been found, but not all were chemically identified. Looking for the source of radioactivity of uranium Sir William Crookes in London extracted the uranium from a pure uranium nitrate hexahydrate by ether and found the radioactivity in the aqueous residue from which he could co-precipitate it together with iron hydroxide by ammonia. After many experiments he was not able to find any similarity with a known chemical element. He wrote: „For the sake of lucidity the new body must have a name. Until it is more tractable I will call it UrX – the unknown substance in uranium". [27] Now we know, that his UrX consists of ^{234}Th and its daughter ^{234m}Pa which decays to ^{234}U, and the radioactive substance discovered in the same year by Debierne contained mainly ^{230}Th, the daughter of ^{234}U and mother of ^{226}Ra. Both radioactive substances discoverd by Crookes and Debierne are isotopes of thorium which are members of the decay series of ^{238}U.

The similarity of some radioactive elements became obvious after the discovery of Radiothor (^{228}Th) by Otto Hahn in 1905 when he separated radium from a thorium rich mineral. Frederick Soddy who created the name isotopes, said in his Nobel lecture: "The history of isotopes fittingly commences with the discovery of radio-thorium, a new product of the thorium disintegration seris." Radiothor was found to be similar with the well known thorium by a lot of scientists. In 1907 McCoy and Ross had unsuccessfully tried to separate both. They wrote: „Our experiments sharply indicate that the radiothor is entirely inseparable from thorium by chemical processes".[28] In 1913 Soddy named these chemical inseparable elements isotopes [29] which were explained in detail by Georg de Hevesy and Fritz Paneth. They wrote, that isotopes are able to replace each other in chemical procedures, but

[25] Lavoisier A.: Elements of Chemistry, translated by Robert Kerr, in the Great book of the Western World, 2nd Edition, Chicago (1990)
[26] Curie M., Curie P., Bemont G.: Sur une nouvelle substance fortement radio-active, contenue dans la pechblende, C. r. 127, 1215-1217 (1898b)
[27] Crookes W.: Radio-activity of Uranium, Proc. R. Soc. Lond. 66, 409-423 (1899)
[28] McCoy H. N., Ross W. H.: The speific radioactivity of thorium and the variation of the activity with chemical treatment and with time. J. Am. Chem. Soc. 29, 1709-1718 (1907)
[29] Soddy F.: The Origin of Actinium. Nature 91, 634-635 (1913)

nevertheless there is a principal possibility for their separation using the differences in their masses e.g. by diffusion and centrifugation. [30]

The late acceptance of Giesels discovery

Giesel was not accepted as discoverer of actinium for a long time, because at the time of his discovery in Germany no famous expert in the field of radioactivity was able to confirm it. When Giesel in May 1904 had visited Paris, the Curie`s were well known scientists worldwide. Their scientific results have been presented in the weekly sessions of the French Academy of Sciences a half year before they have been awarded with the Nobel Prize together with Henri Becquerel. Since 1899 Debierne has been an assistant of Pierre Curie at the Sorbonne. In consideration of the high authority of the Curies doubts about the results of Debierne did not gain any hearing. Susan Quinn wrote in a biography about Marie Curie that Debierne was a close friend of the family and had spent much time with them. She did not mention that Debierne had discovered actinium.[31] Giesel was an excellent chemist, knowing nearly all papers about radioactivity. He was in good contact with many scientists. In the first years he was the only one able to supply other researchers with high quality radium preparations. In 1903 William Ramsay and Frederick Soddy got from him a sample of 30 mg. With this they found the production of helium from radium. Nevertheless in the scientific community the reward of his position as chemist in a factory was not comparable with that of a professor at a university. When Otto Hahn and Lise Meitner were looking for the precursor of actinium in residues of the production of radium from uranium minerals they obtained specially enriched preparations according the order of Hahn und Meitner from Giesel. In this material Lise Meitner enriched the long–lived isotope of the element protactinium together with tantalum, in which after a decay time she could measure actinium. [32] In spite of the important contribution of Giesel to the discovery of the precursor of actinium Hahn and Meitner could nothing do for the acceptance of Giesel as discoverer of actinium during World War I. Later Debierne became an important person as head of the Radium Institute in Paris, member of the Académie française and member of the International Committee on Atomic Weights.

Doubts that Debierne has discovered actinium with the atomic number 87 are expressed 25 years after World War II. The radio chemist Harold W. Kirby wrote in 1971 that Debierne´s claim to priority is based on two papers which are, as Boltwood said later were characterized

[30] Hevesy G., Paneth F.: Zur Frage der isotopen Elemente. Physik. Z. 15, 797-805 (1914)
[31] Quinn S.: Marie Curie: A Life. Da Capo Press, 1995, transl. in German by König I., Marie Curie – eine Biographie, Insel-Verlag, Frankfurt a. M. 1999, pp 183
[32] Hahn O, Meitner L: Die Muttersubstanz des Actiniums, ein neues radioaktives Element von langer Lebensdauer. Physik. Z. 19, 208-218 (1918)

by the lack of precise experimental details and the absence of explicit statements.[33] In 1996 Jean-Paul Adloff wrote: „In fact Debierne's assertion was false. To our knowledge it appears that his substance was a mixture of the two thorium isotopes ionium (^{230}Th) and radioactinium (^{227}Th) with a small amount of the now known actinium. The error was quite understandable, however owing to the extreme complexity of the mixture of the natural radionuclides. The real discoverer of actinium was probably Giesel. In the light of our knowledge of actinium chemistry, it now appears likely that Debierne´s preparation contains no actinium at all and that his 1900 preparation was a mixture of several radioactive elements possibly including actinium as a minor constituent". [34] A critical reexamination of the evidence, long overdue, leads inevitably to the conclusion that it was Giesel, not Debierne who discovered actinium. [35] In a survey about the discovery of isotopes of actinium is written, that in 1902 Friedrich Oscar Giesel has found a radioactive substance, which he two years later named emanium, now known as ^{227}Ac [36] Nevertheless, even today the French chemist André-Louis Debierne is often called as discoverer of actinium. Therefore it is necessary to appreciate Giesel as discoverer of actinium, like it is written on his gravestone in Brunswick, Germany.

[33] Kirby H. W.: The discovery of actinium, Isis 62, 3 (1971) 290 - 308
[34] Adloff J.-P.: 100 Years after the discovery of Radiochemistry, Oldenbourg Verlag, München 1966
[35] Adloff J.-P.: The centenary of a controversial discovery: actinium, Radiochimica Acta 88, 123 (2000).
[36] Fry C. C., Thoennessen M.: Discovery of the actinium, thorium, protactinium and uranium isotopes.