changes in the habits of mankind. Finally let us plan nationally so as to secure the best of our country, but not forgetting the world as a whole.

Wordsworth has truthfully said,

> . . . To the solid ground
> Of Nature trusts the mind that builds for aye,

and in planning the land for the future we must not neglect the steady solid work of inquiry which can not be done in a day or a decade and for the pursuit of which our universities and colleges need every encouragement. Then let us be reminded by the doggerel of at least one of the world's great troubles of the present day:

> The World is a bundle of hay,
> Mankind are the asses who pull
> But each tugs in a different way. . . .

If we plan efficiently and pull together there is plenty of hay for all.

ELEMENT 91

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THE announcement at the recent meeting of the American Chemical Society in Cleveland of the isolation of 0.1 grams of protactinium oxide and the preparation of metallic element 91 has aroused quite a wide interest in this new element, and it is with pleasure that I follow the suggestion of SCIENCE to write an article on this subject.

(1) INTRODUCTION

The existence of an element between thorium and uranium was predicted in 1869, with the genesis of the greatest generalization of chemistry in the last century—the periodic system of the elements of D. Mendeléeff, whose centenary of birth is now being celebrated.

This element—*ekatantalum* in Mendeléeff's nomenclature, or *Element 91,* according to its number in his system—is now represented by three natural radioactive atomic species or isotopes, to which very recently one, or perhaps two, artificial radioactive species have been added (see Table I).

Chemically, all these species are indistinguishable and behave absolutely alike, so that the chemical properties of Element 91 can be inferred from any one of them; their radioactive or nuclear properties, however, are widely different.

The first representative of Element 91 was discovered in 1913 by K. Fajans and O. Göhring in the form of the rapidly decaying *brevium,* with an average life of its atom = 100 sec. All other isotopes of ekatantalum have also a very short life and are characterized by the emission of negative electrons, with the exception of protactinium which emits -particles, and which is the most important because of its long life.

It was in 1917 that Frederick Soddy, the distinguished pioneer in radioactivity, in collaboration with J. A. Cranston in England and simultaneously and independently O. Hahn and L. Meitner, the leading radiologists in Germany, obtained preparations which gradually transformed into actinium and discovered new alpha rays, which could be due only to a new isotope of Element 91, subsequently named protactinium, present in great dilution in their material.

During the following 10 years all efforts to obtain and isolate the very rare protactinium were unsuccessful, owing to wrong chemical properties being attributed to it, and until 1927 nobody actually saw it or any of its pure compounds. It was generally thought that Element 91 resembles tantalum, just as radium resembles barium; since the latter are always associated in analytical operations, attempts were made to isolate protactinium by adding tantalum to the raw material and extracting them together.

We have to expect, however, for Element 91, according to the periodic law, besides properties similar to tantalum and columbium, also other *individual* and *characteristic* properties, *differing* from its analogues, which should simplify the isolation of the element. Basing himself on these considerations, the writer had the good fortune of extracting in 1927 in pure form the first two milligrams of the pentoxide of protactinium—Pa_2O_5; we attribute this result solely to the great guiding force of Mendeléeff's principle.[1]

In 1928 a technical process of extraction was worked out, and thanks to the help of the I. G. Farbenindustrie A. G. about one half a ton of radium residues could be worked up at their factory in Ludwigshafen on the Rhine and about 40 milligrams of Pa_2O_5 were obtained. From then on our efforts were concentrated on the production of larger quantities of the element for the study of its properties.

(2) CHEMICAL PROPERTIES OF EKATANTALUM AND ITS COMPOUNDS

Mr. M. Agruss and the writer[2] have recently obtained over 0.1 gram of protactinium oxide (see sec-

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[1] A. V. Grosse, *Nature,* 120: 621, 1927; *Naturwissenschaften,* 15: 766, 1927.

[2] A. V. Grosse and M. S. Agruss, *Jour. Am. Chem. Soc.,* 56: 2200, 1934.

tion 6), which allowed the preparation of new compounds and the metal itself. The following is a brief résumé of the compounds known.

Metallic ekatantalum (Et) is a silvery gray shiny metal. In contrast to radium it does not tarnish or oxidize in air. It can be prepared by vacuum cracking of its halides on a tungsten filament at high temperatures, according to the equation:

$$2\,EtX_5 \rightarrow 2\,Et + 5\,X_2 \uparrow (X = \text{Halogen})$$

or by electron bombardment of the oxide.

Ekatantalum pentoxide—Et_2O_5—is a perfectly white powder, with a high melting point. It is a weak base and forms salts with acids. It is easily soluble in 50 per cent. hydrofluoric acid; on evaporating this solution *ekatantalum fluoride hydrate* is obtained in colorless crystals. It forms with potassium fluoride the double salt, *potassium ekatantalum fluoride* K_2EtF_7, which crystallizes in long beautiful needles.

The pentachloride—$EtCl_5$—sublimes also in long, colorless, shiny, needle-like crystals, melting at 301° C. It can be easily obtained according to the equation:

$$Et_2O_5 + 5\,COCl_2 \rightarrow 2\,EtCl_5 + 5\,CO_2$$

at 550° C; at the same time small amounts of an oxychloride with a much higher melting point ($EtOCl_3$?) is also formed.

The pentachloride is hydrolyzed by water into hydrogen chloride and the oxide hydrate. It can be converted into the *bromide* or *iodide* by heating with the corresponding hydrogen halide or alkali halides.

The most characteristic analytical reaction of Element 91 consists in its coprecipitation with zirconium or hafnium phosphate from highly acid solutions.

The atomic weight of *protactinium* was found to be 231 ± 0.5 by converting K_2PaF_7 into Pa_2O_5. The ratio of the masses of $K_2PaF_7 : Pa_2O_5$ was found to be 1.6332 and 1.6323.[3]

(3) THE RADIOACTIVE PROPERTIES OF THE ISOTOPES OF ELEMENT 91

The general radioactive properties of all known isotopes are correlated in Table 1.

TABLE 1

ISOTOPES OF ELEMENT 91

	Name of isotope	Symbol	Atomic weight	Average life	Half-period	Nature of rays	Remarks
	Natural isotopes						
1	Brevium or Uranium X_2	Bv UX_2	234	1.65 min.	1.14 min.	β	Discovered by Fajans in 1913
2	Protactinium	Pa	231	46000 years	32000 years	α(β + γ)	
3	Uranium Z	UZ	234	9.7 hours	6.7 hours	β	Discovered by Hahn in 1921
	Artificial isotopes						
1	Radio-brevium I*	RmI	238? 235?	19 min.	13 min.	β	Considered to be element 93 by Fermi & coworkers
2	Radio-brevium II	RmII	238? 235?	130–145 min.	90–100 min.	β	

* See A. V. Grosse and M. S. Agruss, *Phys. Rev.*, 46: 241, 1934.

It is immediately seen that protactinium occupies an exceptional position, as it is the only one with a sufficiently long life which enables it to be isolated. Like radium it emits nuclei of helium atoms or α-particles, negative electrons or β-particles and γ-rays. Like radium it disintegrates through a whole number of radioactive elements, the so-called actinium series, into the final stable product—actinium lead (see Table 4).

The properties of the rays of protactinium and radium proper are compared in Table 2.

TABLE 2

COMPARISON OF THE PHYSICAL PROPERTIES OF PROTACTINIUM AND RADIUM

Properties	Protactinium	Radium
Average life of atom in years	46,000	2,500
Half-period in years	32,000	1,600
Alpha rays:		
Range in centimeters in air at 760 mm and at 15° C.	3.673	3.389
Velocity in kilometers per second	15,500	15,100
Energy in volts	2,540,000	2,365,000
Beta rays:		
Maximum energy in volts	318,200	185,000
Gamma rays:		
Wave length of the most penetrating ray in 10^{-11} cm	38.2	66.0
Maximum energy in volts	323,000	187,000

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[3] A. V. Grosse, *Jour. Am. Chem. Soc.*, 56, 2501, 1934.

In this connection it should be stressed, however, that the present use of radium in medicine is chiefly due to the γ-rays of its disintegration products (RaB and RaC, C′, C″ from radium emanation), which have a much greater penetrating power than either protactinium or radium proper. Besides, the accumulation of disintegration products in protactinium or radium takes place with widely different rates; radium reaches equilibrium with its products or its maximum activity in about 25 days, whereas for protactinium half of the maximum is reached only in about 15 years.

(4) OCCURRENCE IN NATURE AND ORIGIN

Protactinium occurs in nature always together with radium. It was originally thought that protactinium is much rarer than radium, but recent investigations show that for every 10 grams of radium 8 grams of protactinium are found, no matter what the ore or mineral is.

Since both these radio elements have a very short life compared to the age of our earth, they would have died out long ago had it not been for the fact that they are continuously being formed from the element uranium, although from two different isotopes. The isotope from which protactinium originates is called actino-uranium (symbol = AcU); it has an average life of 650 million years.

For the reasons given above protactinium and radium are found in every mineral or rock containing uranium and in quantities proportional to the uranium content. In the following table analyses of different uranium minerals are given.

TABLE 3

PROTACTINIUM AND RADIUM CONTENT OF MINERALS

(1 metric ton = 1.000.000.000 milligrams)

	Name of mineral	Location	Uranium content in per cent.	Radium content in milligrams per met. ton	Protactinium content in milligrams per met. ton
1	Carnotite	Colorado, U. S. A.	19.09	64.0	52.0
2	Pitchblende	Wilberforce, Canada	52.71	178.0	144.0
3	Kolm	Gullhogen, Sweden	0.41	1.4	1.1
4	Pitchblende	Katanga, Africa	72.26	244.0	198.0
5	Pitchblende	Morogoro, East Africa	70.45	237.0	192.0

(5) THE DISINTEGRATION PRODUCTS OF PROTACTINIUM

The products of protactinium disintegration, their average and half lives, the nature of rays emitted and their chemical properties are given in Table 4.

Actinium or Element 89 is the first disintegration product of protactinium and was discovered by A. Debierne very shortly after the discovery of radium by the Curies. It has never been obtained in a greater concentration than about 1 part in 100,000 and Madame M. Curie devoted much of her time to this element in the last years of her life, because of its interest to medicine. The α-activity of actinium, in equilibrium with all its disintegration products, is about 140 times greater than that of the same quantity of radium.

Now that pure protactinium is available the isolation of actinium is just a question of time; one has only to let a protactinium preparation stand for a year or two and then separate the accumulated actinium.

(6) TECHNICAL EXTRACTION

Thanks to the energy and skill of Mr. M. S. Agruss and based on the experience obtained in the extraction of the first 40 mg of protactinium (see introduction), a technical process for protactinium production was installed and made to operate on a semi-commercial scale. Through the courtesy of the Lindsay Light Company and with the assistance of Dr. Mark Eichelberger the facilities of their plant in West Chicago was made available for this purpose.

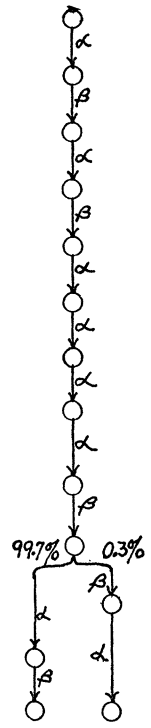
The best starting material is the so-called "residue of residues" (containing on the average 60 per cent. SiO_2, 20 per cent. Fe_2O_3, 7 per cent. PbO and smaller amounts of many other elements), discarded from the process of radium extraction and of no commercial value at present; it contains about 0.30 grams Pa per metric ton. About 5 tons of these residues were bought at a reduced price and exchanged for patent rights from the Czechoslovakian Government, which owns the oldest radium factory in the world at Joachimsthal, Bohemia. The negotiations carried on for this purpose were successful largely due to the efficient support of Mr. A. C. Ratchesky, U. S. Minister to Czechoslovakia, and Mr. Frank Novotny, of the U. S. Legation in Prague.

The process involves the use of only two major chemicals, muriatic acid and flake caustic soda. The principle of the process can best be seen from Fig. 1.

The plant product, containing an average of 1 part

TABLE 4

THE ACTINIUM RADIO-ACTIVE SERIES

Radio-element and symbol	Atomic number	Isotopic with	Atomic weight	Type of disintegration	Half-period	Scheme of distintegration
Actino-uranium, AcU	92	U	235	Alpha	4.0 . 10^8 yrs.	
Uranium Y, UY	90	Th	231	Beta	24.6 hours	
Protactinoum, Pa	91	Et	231	Alpha	32,000 years	
Actinium Ac	89	Ac	227	Beta	13.4 years	
Radio-actinium, Ra-Ac	90	Th	227	Alpha	18.9 days	
Actinium X, AcX	88	Ra	223	Alpha	11.2 days	
Actinon or Actinium Emanation, Ac-Em	86	Em	219	Alpha	3.92 seconds	
Actinium A, AcA	84	Po	215	Alpha	0.002 seconds	
Actinium B, AcB	82	Pb	211	Beta	36.0 minutes	
Actinium C, AcC	83	Bi	211	Alpha and Beta	2.16 minutes	
Actinium C′ AcC′	84	Po	211	Alpha	ca. 0.005 sec.	
Actinium C″, AcC″	81	Tl	207	Beta	4.76 minutes	
Actinium Lead or Actinium D AcD	82	Pb	207	......	Stable	

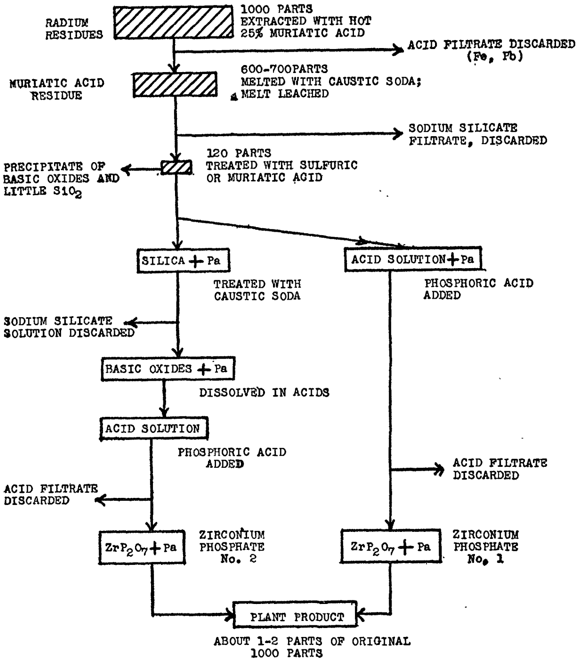


FIG. 1. Scheme of technical protactinium extraction process.

in 5,000 of protactinium, is further concentrated in the laboratory by means of the spiral process, as illustrated in Fig. 2.

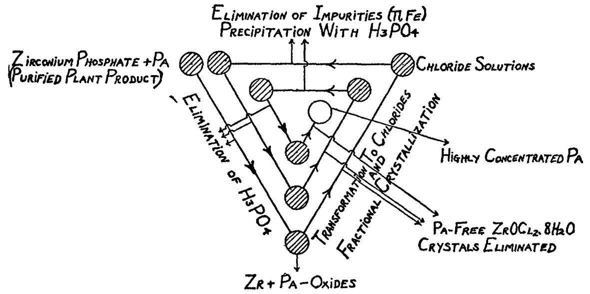


FIG. 2. Spiral concentration process.

In this way preparations containing 10 per cent. protactinium are obtained, from which the pure compounds of the element can be easily isolated.

Up to the present moment about 0.20 grams protactinium oxide were obtained either in the pure or highly concentrated state.

Recently our technical and laboratory process has been successfully used in Germany by Drs. G. Graue and H. Käding[4] and about 0.70 grams of protactinium isolated from about 5 tons of radium residues. The figures for the present "world production" are correlated in Table 5.

TABLE 5

Year	Amount of Pa in milligrams	Remarks
1927	2	
1928	40	At the I.G. Farbenindustrie A.G., in Ludwigshafen on the Rhine.
1934	700	by G. Graue and H. Käding.
1934	200	at Lindsay Light Co., in West Chicago, Ill.

The total quantity of protactinium available at the end of this year will be over 1 gram.

(7) Artificial Isotopes. (Fermi's Element 93)

Experiments carried out this year by E. Fermi and his coworkers[5] in Italy on the bombardment of uranium with neutrons have led him to believe that artificial elements with an atomic number of 93 and 94 have been formed. Particularly the β-ray emitting product from uranium with a half period of 13 minutes and, very recently, the 90–100 minute element were assumed to be isotopes of element 93 because of the similarity of their reactions with manganese[5] and rhenium (element 75)[6] and their dissimilarity from the heaviest elements.

In collaboration with Mr. M. S. Agruss these reactions were repeated with protactinium and found to be both qualitatively and quantitatively identical with those of Element 91.[7]

Whereas Fermi's interpretation of the neutron bombardment can be expressed by the nuclear equation:

$$U^{238}_{92} + {}_0n^1 \longrightarrow 93^{239} + \varepsilon^- \longrightarrow 94^{239}$$

leading to elements 93 and 94, our results force us to conclude that Element 91 is being formed either according to reaction A or B:

$$ {}_{92}U^{238} + {}_0n^1 \longrightarrow {}_{91}Et^{238} + {}_1H^1; \quad {}_{91}Et^{238} \xrightarrow{\beta} {}_{92}U^{238} \ldots\ldots\ldots A$$

$$ {}_{92}U^{238} + {}_0n^1 \longrightarrow {}_{90}Th^{235} + {}_2He^4;$$

$$ {}_{90}Th^{235} \xrightarrow{\beta} {}_{91}Et^{235} \xrightarrow{\beta} {}_{92}U^{235} \ldots\ldots\ldots B$$

If these interpretations are correct they point a way to the synthetic production of the fourth and as yet unknown radioactive series, with atomic weights $= 4n + 1$ (n being any whole number), by neutron bombardment of members of the thorium series, as exemplified by the equation:

$$ {}_{90}Th^{232} + {}_0n^1 \longrightarrow 88^{229} + {}_2He^4; \quad 88^{229} \xrightarrow{\alpha \text{ or } \beta} \text{fourth series.}$$

(8) Future Practical Application

What are the practical uses of Element 91?

It is yet premature to answer this question. Because of its chemical properties, dissimilar to radium, protactinium might find an application in radiology and medicine, different from radium; also constant formation of actinium might be of large practical value. Perhaps the stability in air of the metal or the possibility of plating other metals with it (radio tubes?) will be found useful. We are confident that it will find an application in the future like most of the rare elements; as an example we may remember the case of neon. Twenty-five years ago it was one of the rarest gases in the atmosphere; now its light illuminates the skies.

(9) Acknowledgments

These investigations, and particularly the extraction of protactinium from radium wastes, required by their very nature large financial expenditures. It was possible to accomplish the work through a generous grant by Mr. Hiram J. Halle, of New York City, to whom we express our sincere gratitude.

We are also much indebted to Professor Julius Stieglitz, of our department, for his continuous help and advice; to Dr. Gustav Egloff for the privilege of using the facilities of the Research Laboratories of the Universal Oil Products Company, and to Surgeon General Hugh S. Cumming, of the U. S. Public Health Service, for his early interest and encouragement.

OBITUARY

BAILEY KELLY ASHFORD

In the death of Dr. Bailey Kelly Ashford at his home in San Juan, Puerto Rico, on November 1, 1934, tropical medical science loses a distinguished investigator and an eminent physician.

Son of a well-known physician and surgeon, Dr. Bailey Ashford was born on September 18, 1873, in the city of Washington. He left George Washington University in his junior year, took up the study of medicine in the Georgetown Medical School and graduated therefrom in the year 1896. The following two

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[4] G. Graue and H. Käding, *Naturwissenschaften*, 22: 386, 1934.

[5] See E. Fermi, *Nature*, 133: 898, 1934.

[6] E. Fermi, E. Amaldi, O. D'Agostino, F. Rasetti and E. Segrè, *Proc. Roy. Soc.*, A. 146: 495, 1934.

[7] A. V. Grosse and M. S. Agruss, *Phys. Rev.*, 46: 241, 1934; results with rhenium yet unpublished.