THE SYNTHETIC RADIOACTIVE ISOTOPES OF THE LESS FAMILIAR ELEMENTS[1, 2]

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The phenomenon of radioactivity was first observed by Becquerel in 1896 while he was working with compounds of uranium (4). Subsequent research by many investigators revealed more than forty atomic species having the property of spontaneously disintegrating by emitting charged particles. In 1919 Rutherford showed that it was possible to disintegrate stable nuclei by bombarding them with energetic alpha particles from natural radioactive sources (31). However, it was not until 1934 that radioactive isotopes were synthesized. At that time, Curie and Joliot observed exponentially decaying positron activities in boron, magnesium, and aluminum when these elements were bombarded with alpha particles (13). Since then, about two hundred radioactive isotopes of eighty-five of the chemical elements have been reported (26). The synthesis of radioactive elements by bombardment with alpha particles immediately suggested the use of other projectiles in effecting this type of synthesis. Deuterons, protons, neutrons, and gamma rays have all proved effective in bringing about the nuclear transformations necessary for the production of radioactive isotopes of the stable elements. These types of reaction will be briefly outlined.

METHODS OF PRODUCTION OF ACTIVE ISOTOPES

1. Alpha particles

Natural radioactive disintegrations furnish alphas of energies up to 8.8 M.e.v. which are very useful in producing radioactivity in the light elements (20). These are effective on elements up to calcium, whose atomic number is 20. Low intensity and limited energy are the most serious

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drawbacks for this type of projectile. Recent work with $_2He^4$ ions accelerated in the cyclotron indicates that the use of alphas can be extended indefinitely. Radioactive isotopes of elements of atomic number up to 53 have already been produced by this means (22, 23, 34).

The capture of alpha particles with the simultaneous emission of protons or neutrons results in nuclei which are radioactive. In the first case the resulting nuclei exhibit both electron and positron activities, but in the second case only positron activities are observed.

2. Protons

Hydrogen ions, accelerated by any of the several methods available, can be used in producing nuclear reactions that lead to radioactive isotopes of the stable elements (11). This type of projectile has been most effective for light elements, but the use of more energetic protons from the cyclotron has already led to reactions involving elements of high atomic number (8).

Proton capture also follows two types of reactions. The first is accompanied by the emission of neutrons and yields nuclei that are electron- or positron-active. The second type does not involve a simultaneous particle emission but involves the emission of gamma rays, leaving nuclei that are positron-active.

3. Deuterons

More effective than protons or alphas for producing radioactive isotopes of the stable elements are deuterons. Because they have a smaller charge, penetration into the nucleus is easier than for alphas. At high energies they can split at the nucleus, allowing their neutron component to enter the nucleus while the proton component is repelled by the nuclear field (28). The energy necessary to effect nuclear transformations can be given these particles by any of the methods used for accelerating ions.

Most deuteron reactions are accompanied by simultaneous emission of alphas, protons, or neutrons. In the first two classes the residual nuclei can be electron- or positron-active; in the third class the nuclei are only positron-active.

4. Neutrons

Most effective of all particles for producing radioactive nuclei of the stable elements are neutrons (19). Fermi first used them for this purpose and showed that they induce activities in nearly all elements. Their great effectiveness lies in the fact that these particles have no nuclear charge, hence there is no Coulomb force opposing their entry into the nuclei of atoms. The neutrons used must be produced by some nuclear reaction, several of which are suitable. Alphas from radium and its decay products give fast neutrons from beryllium and less energetic neutrons from boron (9, 13, 17). The reaction of deuterons on deuterium furnishes a source of monoenergetic fast neutrons (5). A very intense source of neutrons is obtained by the action of deuterons on beryllium (12).

Neutron reactions fall into four classes: alphas, protons, gamma rays, or two neutrons may be products of the initial disintegration. The residual nuclei may then decay with the emission of electrons in the first three cases and either electrons or positrons in the fourth.

5. Gamma rays

Disintegration by gamma rays was first observed by Chadwick and Goldhaber, using gamma rays from ThC″ with ${}_1H^2$ (10). These natural gamma rays will also disintegrate ${}_4Be^9$, but are not effective on elements of higher atomic number (33). However, gamma rays of 17 M.e.v. are produced in the reaction between protons and lithium, and these very energetic gammas have been used by Bothe and Gentner for inducing radioactivity in elements of atomic number up to 73 (7). The reaction involves absorption of a photon and the emission of a neutron, and leaves nuclei which are either electron- or positron-active. This method of producing radioactive elements is important, for it allows the identification of the active isotope in many cases.

IDENTIFICATION OF ACTIVE ISOTOPES

In nuclear reactions the atomic number Z and the mass number A of bombarding particles are known, Z of the target is known, and A and Z for the lighter disintegration product can be determined. From this data the Z for the residual nucleus can be calculated. If the residual nucleus is radioactive, the value of Z can be checked by chemical separation of the active element and tracing its course with some counting device.

An excellent example of this procedure is found in boron, one of the first elements to be rendered radioactive. Boron bombarded with alphas gives neutrons (6). The resulting material has a single positron activity of 11 min. half-life. The reaction can thus be indicated:

$${}_5B^A + {}_2He^4 \rightarrow {}_0n^1 + {}^{*}_{7}X^{A+3} = {}^{*}_{7}N$$

A target of boron nitride after bombardment with alphas can then be treated with a sodium hydroxide solution which will form ammonia. This gas can be removed from the solution. It is then found that all of the positron activity is in the ammonia and none in the sodium orthoborate solution. In order to show conclusively that the nuclear reaction does not involve nitrogen, targets containing boron but no nitrogen and targets containing nitrogen but no boron can be used. The 11 min. activity will be found in the first target, but only the 70 sec. activity of ${}^{*}_{9}F^{17}$ in the second. This definitely establishes the atomic number of the target and of the residual nucleus.

There is now a final factor to be determined for this reaction, namely, the mass number of the target and product. A table of isotopes will show two isotopes of boron, with masses of 10 and 11. Considering first the most abundant isotope of mass 11, the equation for the nuclear reaction becomes:

$$_5B^{11} + {}_2He^4 \rightarrow {}_0n^1 + {}_7N^{14}$$

But $_7N^{14}$ is a stable isotope and would not emit positrons. If $_5B^{10}$ is taken, the residual nucleus is $_7N^{13}$.

This isotope has not been observed among the stable isotopes of nitrogen and is, therefore, considered the radioactive isotope formed in the reaction. The complete equation is then:

$$_5B^{10} + {}_2He^4 \rightarrow {}_0n^1 + {}^{*}_{7}N^{13} \rightarrow e^+ + {}_6C^{13}$$

The final product, $_6C^{13}$, is a stable isotope.

As a means of correlating the nuclear reactions observed and predicting other reactions, Evans and Livingston devised an isotope chart on which all of the stable isotopes found in nature have been plotted (18). In this chart the atomic numbers, Z, are plotted as abscissae and the "isotope numbers," $A - 2Z$, are plotted as ordinates. This isotope number represents the number of neutrons in the nucleus in excess of the number of protons.

The advantages of using this scale to represent the mass numbers are that the region of stable isotopes is clearly defined, the ordinates give directly the number of excess neutrons necessary for stable nuclei, and the vertical scale is shortened to a convenient length. If a nuclear reaction results in a product nucleus which lies above the region of stable isotopes, the nucleus will come back into that region by emitting an electron. If the resulting nucleus is below the region of stable isotopes, it will become stable by emitting a positron.

As an aid in clarifying nuclear reactions, the isotope chart may be used as follows: Bombardment of manganese and chromium with fast neutrons and vanadium with slow neutrons in each case yields an element which emits electrons (3). The decay period is 3.75 min. for all these targets, hence the product must be the same in all three reactions. In order to determine what is the product and how it is formed, the distribution of the isotopes of these elements must be studied (figure 1). The stable isotopes are $_{23}V^{51}$, $_{24}Cr^{50, 52, 53, 54}$, and $_{25}Mn^{55}$. The only reactions that will account for the results are:

$$\left.\begin{array}{l} {}_{25}\mathrm{Mn}^{55} + {}_{0}n^{1} \rightarrow {}_{2}\mathrm{He}^{4} + {}^{*}_{23}\mathrm{V}^{52} \\ {}_{24}\mathrm{Cr}^{52} + {}_{0}n^{1} \rightarrow {}_{1}\mathrm{H}^{1} + {}^{*}_{23}\mathrm{V}^{52} \\ {}_{23}\mathrm{V}^{51} + {}_{0}n^{1} \rightarrow {}^{*}_{23}\mathrm{V}^{52} \end{array}\right] {}^{*}_{23}\mathrm{V}^{52} \rightarrow e^{-} + {}_{24}\mathrm{Cr}^{52}$$

Chemical tests also indicate that the radioactive element is vanadium.

A similar group of reactions is found with manganese, iron, and cobalt as targets for neutrons.

RADIOACTIVE ISOTOPES AND THE PERIODIC TABLE

The periodic table has four places where the elements have not yet been isolated and identified beyond question. The missing elements are those of atomic numbers 43, 61, 85, and 87.

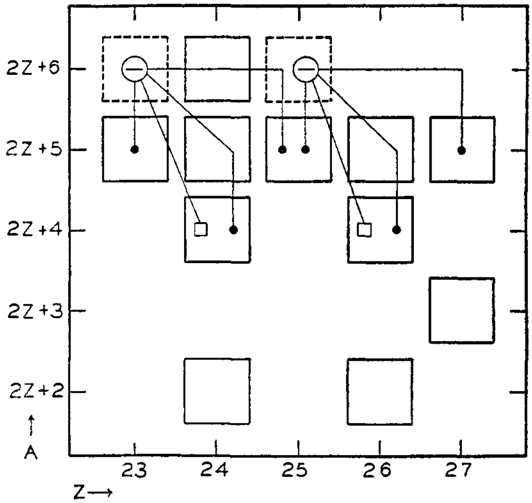

FIG. 1. Distribution of the isotopes of elements of atomic number 23 to 27

It is probable that element 61, illinium, is naturally radioactive. This would account for the difficulty in obtaining it in an appreciable quantity. Samarium is definitely radioactive, emitting alpha particles (15). This activity can be assigned to ${}_{62}\mathrm{Sm}^{152}$ on the basis of studies of the hyperfine structure (32). Beta activity has been detected in neodymium (24). Maurice Curie has reported a beta activity in the middle fractions of a neodymium–samarium mixture which would be most likely to contain element 61 (16). The complete chain of reactions can be represented as:

$${}_{62}\mathrm{Sm}^{152} \rightarrow {}_{2}\mathrm{He}^{4} + {}_{60}\mathrm{Nd}^{148} \rightarrow e^{-} + {}_{61}\mathrm{Il}^{148} \rightarrow e^{-} + {}_{62}\mathrm{Sm}^{148}$$

The discoveries of the other three missing elements have been reported, but the claims have not been definitely established in any case (27, 2, 1).

In order to obtain some idea of their chemical properties, it would be desirable to obtain synthetic radioactive isotopes of these elements.

For element 43, masurium, these have been prepared by the following nuclear reactions (25, 29):

$${}_{44}\mathrm{Ru}^{A} + {}_{1}\mathrm{H}^{2} \rightarrow {}^{*}_{43}\mathrm{Ma}^{A-2} + {}_{2}\mathrm{He}^{4}$$

$${}_{42}\mathrm{Mo}^{A} + {}_{1}\mathrm{H}^{1} \rightarrow {}^{*}_{43}\mathrm{Ma}^{A} + {}_{0}n^{1}$$

$${}_{42}\mathrm{Mo}^{A} + {}_{1}\mathrm{H}^{2} \rightarrow {}^{*}_{43}\mathrm{Ma}^{A+1} + {}_{0}n^{1}$$

There are several other nuclear reactions that would be expected to yield a radiomasurium. These have not been successful to date.

The last of the three reactions above yields a radiomasurium of long half-life (several weeks). This activity has been used in the investigation of the chemical properties of element 43 (29).

Using a piece of molybdenum bombarded for several months by high energy deutrons from the Berkeley cyclotron, Perrier and Segrè have shown that the long-life electron activity is due to element 43. Chemical separations eliminated molybdenum, columbium, zirconium, and ruthenium, leaving only masurium as the possible carrier of the activity.

When manganese and rhenium are added to solutions containing the radiomasurium, the activity is found to follow rhenium much more closely than manganese. The characteristic reactions of rhenium were also characteristic of masurium with one exception. Concentrated sulfuric acid (80 per cent) containing rhenium and radiomasurium remained active when moist hydrogen chloride was passed through the solution. The rhenium was carried out by the gas stream. This was the only chemical reaction resulting in an appreciable separation of the two elements.

A study of the isotope chart indicates one possible reaction of all the types now known that would produce element 85 (figure 2). Bismuth has one stable isotope, ${}_{83}\mathrm{Bi}^{209}$. If this were bombarded with very energetic alphas, element 85 might be produced according to the reaction:

$${}_{83}\mathrm{Bi}^{209} + {}_{2}\mathrm{He}^{4} \rightarrow {}_{0}n^{1} + {}^{*}_{85}\mathrm{X}^{212} \rightarrow e^{+} + {}_{84}\mathrm{ThC}'^{212}$$

The resulting nucleus should be positron-active, since it lies below the region of naturally occurring isotopes. The testing of this reaction must wait until instruments for the production of extremely energetic alphas are available.

There are two possible reactions for the production of a synthetic radioelement 87 (figure 2). The probability of these ever being tried are very slight, however, since the practical difficulties involved are almost insurmountable. The only target material available for the reaction is radium.

Expense, danger of handling, and experimental difficulties due to natural decay products make this possibility one of theoretical interest only. The nuclear reactions mentioned are:

$$
{}_{88}\mathrm{Ra}^{221} + {}_{0}n^{1} \rightarrow {}_{1}\mathrm{H}^{1} + {}_{87}\mathrm{X}^{226} \rightarrow e^{-} + {}_{88}\mathrm{Ra}^{226}
$$

$$
{}_{88}\mathrm{Ra}^{226} + {}_{1}\mathrm{H}^{2} \rightarrow {}_{2}\mathrm{He}^{4} + {}_{87}\mathrm{X}^{224} \rightarrow e^{-} + {}_{88}\mathrm{ThX}^{224}
$$

Among the nuclear reactions of the less familiar elements that are of unusual interest are those involving bismuth, thorium, and uranium. The first of these elements, bismuth, gives with deuteron bombardment a radioactive product that is identical with RaE, a natural radio-isotope of bismuth (25). The reaction is (figure 2):

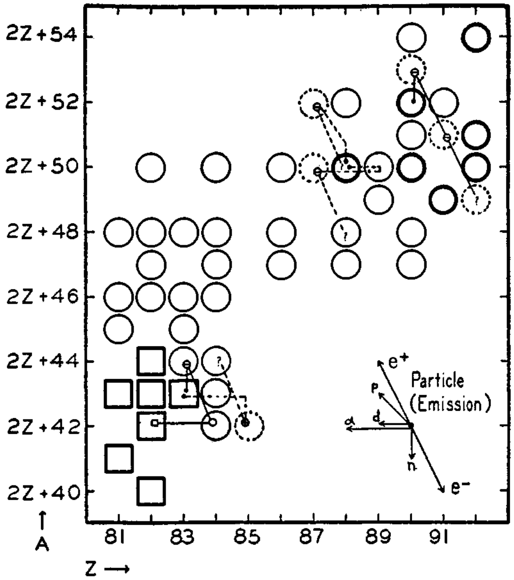

FIG. 2. Distribution of the isotopes of elements of atomic number 81 to 92. Solid circles represent natural radioactive isotopes. Heavily outlined isotopes are of elements which can be separated in weighable amounts.

$$
{}_{83}\mathrm{Bi}^{209} + {}_{1}\mathrm{H}^{2} \rightarrow {}_{1}\mathrm{H}^{1} + {}_{83}\mathrm{RaE}^{210} \rightarrow e^{-} + {}_{84}\mathrm{RaF}^{210} \rightarrow {}_{2}\mathrm{He}^{4} + {}_{82}\mathrm{RaG}^{206}\ (\mathrm{Pb})
$$

Thorium and uranium both lead to new radioactive series on bombardment with neutrons. In this way they differ from the lighter radioactive elements which give stable isotopes upon decay.

The synthetic radioactivity in thorium has been carefully studied by Curie, Halban, and Preiswerk (14). They have identified by chemical tests the four active products and have established a genetic relationship

TABLE 1

*A selected list of synthetic radioactive isotopes of the elements**

ATOMIC NO.	SYMBOL	ACTIVITY	HALF-LIFE	ATOMIC NO.	SYMBOL	ACTIVITY	HALF-LIFE
6	C	e^+	20.5 min.	48	Cd	e^-	4.3 hr.
7	N	e^+	11 min.	49	In	e^-	2.3 hr.
9	F	e^+	112 min.	50	Sn	e^-	28 hr.
11	Na	e^+ and e^-	6 months and	51	Sb	e^-	2.5 days
			14.8 hr.	52	Te	e^-	1 hr.
14	Si	e^-	170 min.	53	I	e^-	25 min.
15	P	e^-	14.5 days	55	Cs	e^-	1.5 hr.
16	S	e^-	80 days	56	Ba	e^-	85.6 min.
17	Cl	e^+	37 min.	57	La	e^-	31 hr.
18	A	e^-	110 min.	59	Pr	e^-	19 hr.
19	K	e^-	12.2 hr.	60	Nd	e^-	1 hr.
20	Ca	e^-	2.4 hr.	62	Sm	e^-	2 days
21	Sc	e^+	52 hr.	63	Eu	e^-	9.2 hr.
23	V	e^+	16 days	64	Gd	e^-	8 hr.
25	Mn	e^+	5 days	65	Tb	e^-	3.9 hr.
26	Fe	e^-	40 days	66	Dy	e^-	2.5 hr.
27	Co	e^-	1 year	67	Ho	e^-	35 hr.
28	Ni	e^+	3 hr.	68	Er	e^-	12 hr.
29	Cu	e^+ or e^-	12.8 hr.	69	Tm	e^-	8 months
30	Zn	e^-	100 hr.	70	Yb	e^-	3.5 hr.
31	Ga	e^-	23 hr.	71	Lu	e^-	6 days
32	Ge	e^-	30 min.	72	Hf	e^-	1 month
33	As	e^-	26 hr.	73	Ta	e^-	200 days
34	Se	e^-	56 min.	74	W	e^-	23 hr.
35	Br	e^-	36 hr.	75	Re	e^-	20 hr.
37	Rb	e^-	22 hr.	76	Os	e^-	40 hr.
38	Sr	e^+	3 hr.	77	Ir	e^-	3 days
39	Y	e^-	70 hr.	78	Pt	e^-	14.5 hr.
40	Zr	e^-	40 hr.	79	Au	e^-	2.7 days
42	Mo	e^-	36 hr.	80	Hg	e^-	40 hr.
43	Ma	e^-	46 days	81	Tl	e^-	1.3 hr.
44	Ru	e^-	11 hr.	82	Pb	e^-	8.6 days
45	Rh	e^-	1.1 hr.	83	Bi	e^-	5 days
46	Pd	e^-	12 hr.				
47	Ag	e^+	25.5 min.				

* This list is one selected from a complete list (26) of synthetic radioactive elements as of July 1, 1937. The purpose of the selection was to indicate those elements whose half-lives are of sufficient length to make them useful as chemical indicators.

between two of them (figure 2). On this basis they postulated another radioactive series of the type $4n + 1$. Their scheme is:

$$_{92}U^{237} \rightarrow {}_2He^4 + {}_{90}Th^{233} \xrightarrow[25\text{ min}]{} e^- + {}_{91}Pa^{233} \xrightarrow[2.5\text{ min.}]{} e^- + {}_{92}U^{233} \rightarrow$$

$${}_2He^4 + {}_{90}Th^{229} \rightarrow {}_2He^4 + {}_{88}Ra^{225} \rightarrow \text{etc.}$$

In order to see if such a series existed in nature they examined carefully purified uranium and concluded that if it did exist, its abundance was $<1/10{,}000$ of the $4n + 2$ series.

Neutron bombardment of uranium leads to a very complex group of activities which have been thoroughly investigated by Hahn, Meitner, *et al.* (21). Three distinct radioactive series result, all of which lead to elements of successively higher atomic number by electron emisson. This situation is without parallel, as all other series emit alpha particles after one or two beta emissions. Elements to atomic number 96 have been identified by chemical tests, and no evidence of alpha emission has been obtained. These interesting series of nuclear transformations should add much to our understanding of the upper limit of the periodic table (30).

The longer lived synthetic radioactive isotopes of the less familiar elements are given in table 1. Also listed are the radioactive isotopes of the more common elements that have long enough half-lives to make them useful as chemical indicators. Today it is usually possible to obtain from the larger hospitals, for experimental purposes, radon seeds which can be used in radon–beryllium neutron sources. With this source of activation and with the artificial sources available in several of the larger universities, more research should be directed into those fields opened up by the powerful new tool of chemistry, the synthetic radioactive isotopes of the stable elements.

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