RADIOACTIVITY OF THE HEAVY ELEMENTS

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The past few years have seen a rapid expansion of our knowledge of the isotopes of those elements of greater atomic number than gold ($Z \geqslant 79$). These developments include the discovery of new branch modes of decay of members of the three natural radioactive series, giving rise to isotopes of the missing elements astatine ($Z = 85$) and francium ($Z = 87$); the elucidation of several new radioactive decay series derived from synthetic nuclei, including some comprising the missing $4n + 1$ series; and the extension of the decay series to include isotopes of the elements beyond uranium ($Z = 92$) up to californium ($Z = 98$). The speed with which the intricacies of the several collateral series have been resolved is remarkable by comparison with the tortuous unravelling of the natural decay series. It is the purpose of this Review to describe briefly these developments and to show how important the contribution of new techniques, especially of electronic instrumentation, has proved to progress in this field.

Modification of the Natural Decay Series.—The principal problems outlasting the classical studies in the natural decay series were the determination of the origin of the actinium series, together with the identity and relation of uranium-X_1, uranium-X_2, uranium-Y, and uranium-Z, the possible α-activity of actinium, and the apparent absence of a radioactive decay series whose members possessed mass numbers that could be expressed in the form $4n + 1$. The solution of the first of these problems was largely complete before the period under consideration, but it provides a convenient link with the earlier investigations.

Origin of the Actinium Series.—The constant relation between the actinium and the radium family had suggested that the two series were genetically connected.[1] After the discovery of the α-active protactinium announced almost simultaneously by Hahn and Meitner [2] and by Soddy and Cranston,[3] it was surmised that uranium-Y, whose existence was by then amply confirmed [4] and which was presumed to be the parent of the protactinium,[5] must also be the first product of the branching. The most natural junction of the series appeared likely to be U-II.[1] The discovery [6] of another, β-active isotope of protactinium, U-Z, requiring accommodation in one or other of the two series, only lent greater complexity to the problem.

[1] Boltwood, *Amer. J. Sci.*, 1908, **25**, 269; Meyer, Hess, and Paneth, *Ber. Akad. Wiss. Wien*, 1914, **123**, 1459; Kirsch, *ibid.*, 1920, **129**, 309.

[2] *Naturwiss.*, 1918, **6**, 324. [3] *Proc. Roy. Soc.*, 1918, *A*, **94**, 384.

[4] Antonoff, *Phil. Mag.*, 1913, **26**, 1058; Guy and Russell, *J.*, 1923, **123**, 2618.

[5] Antonoff, *Phil. Mag.*, 1911, **22**, 431; Soddy, *ibid.*, 1914, **27**, 215; Gratias and Collie, *Proc. Roy. Soc.*, 1933, *A*, **139**, 567.

[6] Hahn, *Naturwiss.*, 1921, **9**, 84, 236; *Ber.*, 1921, **54**, 1131.

Since neither of the known longer-lived members of the actinium series was available in sufficient quantity, and since the end product, actinium-*D*, was inevitably contaminated with an excess of radium-*G*, the lead isotope terminating the radium series, atomic-weight determinations were of no avail in assigning mass numbers. Indeed, the apparent connection between the radium and actinium series suggested that the latter were also members of the $4n + 2$ series.[7] Nevertheless, the correct values were anticipated by Piccard and Stahel [8] and by Russell,[9] who suggested the series might have its origin in an isotope of uranium of mass number 235. The former authors supposed that the actino-uranium, ^{235}U, was in turn formed from ^{239}U by changes analogous to the formation of U-II from U-I : thus a place in the series could be found to accommodate U-*Z*.

The proof that the series indeed descended from an actino-uranium, ^{235}U, began with the mass-spectrographic analysis by Aston [10] of a sample of radiogenic lead separated from Norwegian broggerite by Piggot.[11] A line due to a lead isotope of mass number 207, of greater intensity than that due to the isotope of mass number 208, was detected. Now, in ordinary lead the 208 line is twice as strong as the 207 line, so that the additional ^{207}Pb in the sample, at the least, must have been radiogenic. There was every reason to identify this isotope of lead with Ac-*D*, and on this assumption Rutherford [12] calculated that the period of the missing actino-uranium must be about 4×10^8 years. The earliest mass-spectrographic analysis of uranium conducted by Aston [13] two years later was insufficiently sensitive to reveal more than the principal isotope, ^{238}U. It was not until a more sensitive mass spectrometer was employed by Dempster that the expected isotope of mass number 235 was detected.[14] Moreover, before success was achieved, the existence of the isotope was supported by additional chemical evidence, *viz.*, a determination of the atomic weight of protactinium made by Grosse,[15] using the macroscopic quantity of the element he had recently separated from pitchblende. The complete isotopic analysis of uranium awaited the investigation of the element by Nier,[16] using his highly sensitive modification of the Dempster mass spectrometer. The possibility of a heavier parent, uranium 239, as suggested by Piccard and Stahel, was not disproved until the synthetic isotope was shown to be β-active by McMillan.[17]

The solution of this problem was closely connected with advances in mass-spectrometric technique and, since the development of the very sensitive Nier type of instrument, the mass spectrometer has found increasing application in the isotopic allocation of radioactive nuclei.[18] It has also been used to determine the exact isotopic composition of macroscopic

[7] Meitner, " Festschrift Kaiser Wilhelm Gesellschaft Forderung Wiss. Zehnjährigen Jubilaum ", 1921, p. 154.
[8] *Physikal. Z.*, 1922, **23**, 1 ; 1923, **24**, 80. [9] *Phil. Mag.*, 1923, **46**, 642.
[10] *Nature*, 1929, **123**, 313. [11] *J. Washington Acad. Sci.*, 1928, **18**, 269.
[12] *Nature*, 1929, **123**, 313. [13] *Ibid.*, 1931, **128**, 725. [14] *Ibid.*, 1935, **136**, 180.
[15] *J. Amer. Chem. Soc.*, 1934, **56**, 2501.
[16] *Physical Rev.*, 1939, **55**, 150. [17] *Ibid.*, p. 510.
[18] Lewis and Hayden, *Rev. Sci. Instr.*, 1948, **19**, 599.

samples rich in a very long-lived isotope,[19] such as ^{14}C or ^{10}Be, and it is thus necessary for the determination of the half-life of such species. Perhaps the most remarkable of such studies so far reported is the direct investigation of the xenon and krypton isotopes formed by the slow-neutron fission of uranium, carried out by Arrol, Chackett, Epstein, and Thode,[20] using a Nier-type instrument and electrometric recording of the ion currents. Other investigators have used photographic recording and have detected the radioactive species by means of a second photographic plate exposed to the radiations emitted by the recording plate. A similar procedure has been employed for the mass assignment of certain isotopes of the heavy elements, including the very weakly active ^{241}Pu,[21] the mercury isomer ^{199}Hg,[22] and recently, ^{241}Am, ^{243}Cm, and ^{244}Cm.[23]

The Isomerism of U-X_2 and U-Z.—Although U-Y was discovered quite early in the history of radioactivity, it is only recently, with the availability of macroscopic samples of substantially pure ^{235}U from the diffusion and electromagnetic separation plants, that its nuclear properties could be determined precisely. Lately, Knight and Macklin [24] have measured the half-life, 25·5 days, and they have shown that the β-rays, of maximum energy 0·21 M.e.v., are followed in less than 1 micro-second by a strongly converted 35 K.e.v. γ-ray. Nevertheless, the position of U-Y in the decay series was unambiguously established as soon as the origin of the actinium series was determined.

The problem of U-Z was not so easily dismissed. An essentially correct interpretation was suggested by Hahn.[25] Although his results were substantiated by Guy and Russell [4] and by Walling,[26] the existence of nuclear isomerism was not entirely accepted until, with the advent of artificial radioactivity, several simpler examples were described. The possibility of nuclear isomerism had been pointed out, however, by Soddy [27] as early as 1917.

In 1935 Fermi [28] and Kurchatov [29] and their respective collaborators showed that the slow-neutron irradiation of bromine gave rise to three different activities, all due to bromine isotopes. Bothe and Gentner [30] found that two of them could also be generated by the photo-disintegration (γ,n) reaction of bromine. Now bromine consists of only two stable isotopes, ^{79}Br and ^{81}Br, so these results require the existence of two forms of ^{80}Br. Further confirmation of the hypothesis was obtained by Fleischmann,[31] who showed that both activities can be generated by resonance neutron capture in bromine.

[19] Norris and Inghram, *Physical Rev.*, 1948, **73**, 350; McMillan, *ibid.*, 1947, **72**, 591.
[20] *Canadian J. Res.*, 1949, **27**, *B*, 757; Epstein, *Proc. Chem. Inst. Canada* (Hamilton Conference), May, 1947, p. 108.
[21] Bartlett and Swinehart, see Nat. Bur. Stand. Circ. 499.
[22] Bergstrom and Thulin, *Physical Rev.*, 1949, **76**, 313.
[23] Reynolds, Hulet, and Street, *ibid.*, 1950, **80**, 467. [24] *Ibid.*, 1949, **75**, 34.
[25] *Z. physikal. Chem.*, 1923, **103**, 461. [26] *Ibid.*, 1931, **14**, *B*, 290.
[27] *Nature*, 1917, **99**, 414, 433.
[28] Amaldi, d'Agostino, Fermi, Pontecorvo, and Segrè, *Ric. Sci.*, 1935, **61**, 581.
[29] Kurchatov, Kurchatov, Myssowski, and Roussinov, *Compt. rend.*, 1935, **200**, 1201. [30] *Naturwiss.*, 1937, **25**, 284. [31] *Z. Physik*, 1937, **107**, 205.

The existence of excited states of nuclei had long been recognised, but it was generally supposed that the decay constants for photon emission by such states implied half-lives of not much greater than 10^{-12} second. Following the discovery of the anomalous bromine activities, however, C. von Weizsäcker [32] advanced a satisfactory explanation of the existence of long-lived excited states, or nuclear isomers. He showed that the half-life of the state increased as the energy of the photon emitted decreased and, more important, it increased by several orders of magnitude for each unit of increase in the difference of the quantum numbers denoting the total angular momenta of the two states. Hence for large spin changes and low energies of excitation, the half-life for photon emission might be several hours or even days. Development of the theory provided a relation between the internal conversion coefficient for the photons, their energy, and the change in angular momentum, as well as an expression for the ratio of conversion in the K and L orbits in terms of the same quantities. (The internal conversion coefficient is the ratio of the number of atoms disintegrating by the ejection of their own orbital electrons, with energy equal to the difference between the transition energy and the binding energy of the electrons concerned, to the number of atoms directly emitting photons.) The last two relations were of particular value in testing the theory, since they are independent of the nuclear model assumed.[33] The explicit expression obtained for the half-life of the excited state, however, depends on the nuclear model involved and the proportions of electric and magnetic multipole radiations emitted. For the liquid-drop model of the nucleus, which has been so successfully developed by Bohr and Wheeler,[34] Lowen obtains the relation [35]

$$\frac{1}{\tau} = \frac{3}{4} \cdot \frac{Z^2 e^2}{c} \cdot \frac{l+1}{Aa^2} \cdot \frac{(a\omega/c)^{2l}}{1^2 . 3^2 \ldots (2l+1)^2}$$

where τ = the mean life, l = spin change, c = velocity of light, Z = atomic number, A = mass number, a = nuclear radius, and e = electronic charge. The relation shows, in addition to the dependence on photon energy and change in angular momentum already described, that the half-life decreases slowly as the mass number increases.

Various possibilities arise if both isomers are potentially β-active. Suppose the decay constant for photon emission or internal conversion is λ_γ, and for β-decay λ_{β_1}, then the half-life observed for the isomer will be given by $\dfrac{\log_e 2}{\lambda_\gamma + \lambda_{\beta_1}}$. The ground state, or less energetic isomer, may have a decay constant for β-emission of λ_{β_2}. If λ_γ and λ_{β_1} differ by more than an order of magnitude, limiting cases will be approached—in the first, when $\lambda_\gamma \ll \lambda_{\beta_1}$, and the isomers decay independently by β-emission ; in the second, when $\lambda_\gamma \gg \lambda_{\beta_1}$, and the excited state decays principally by isomeric transition. In the latter case the two isomers are genetically related.

[32] *Naturwiss.*, 1936, **24**, 813.
[33] Segrè and Helmholtz, *Rev. Mod. Physics*, 1949, **21**, 271.
[34] *Physical Rev.*, 1939, **56**, 426. [35] *Ibid.*, 1941, **59**, 835.

The ^{71}As isomers are examples of the former and the ^{80}Br isomers of the latter variety.

The study of genetically related nuclear isomers has been facilitated by the discovery by Segré, Halford, and Seaborg [36] that internal conversion of γ-radiation usually leads to the breakage of most of the chemical bonds by which the disintegrating atom is bound ; so that if the isomeric transition radiation is strongly internally converted, most of the daughter nuclei break free from their original molecules and, if exchange between the original molecules and the products of their decomposition does not take place, a method for the chemical separation of the less excited isomer may present itself.[37]

The solution of the relation of the U-X_2–U-Z isomers and the completion of their decay scheme required the measurement of β- and γ-ray energies, together with a method for the detection of related nuclear events.

The first electronic device fulfilling the latter requirement was developed by Rossi [38] in 1931, for use in the study of cosmic rays. It was four years later before the coincidence technique was applied by Bothe and von Baeyer [39] to the detection of very rapidly succeeding nuclear transformations, such as the emission of a γ-ray following β-decay, usually in less than 10^{-9} second. These experiments with Ra-B and Ra-C mark the beginning of the study of decay mechanisms. The Rossi circuit has received many modifications and improvements but is still widely employed. The voltage pulses from the detecting devices can be selected by a discriminating stage, consisting essentially of a biased diode, so that only pulses exceeding some predetermined size pass through. The pulses are then treated, if necessary, by a pulse-forming stage where they are differentiated in order to present a sufficiently steeply rising front to the coincidence stage. The pulses are then applied to the control grids of a number of valves, one for each detecting channel, arranged in parallel with a common anode load. If pulses are received at all the control grids, all the valves are cut off and a large pulse is produced in the load, but while one or more valves still conduct, cutting off the remaining valves produces but little effect. The output stage is arranged to trigger only with the large pulse produced by simultaneous events in each detector. Circuits of this kind allow events, recorded as voltage pulses, to be distinguished if they take place as little as 10^{-8} second apart.[40]

Many other forms of coincidence circuit have been described. In one example, pulses from the first detector are applied to the control grid and those from a second detector to the suppressor grid of a pentode valve, biased so that it can only conduct if pulses arrive at both grids simultaneously ; [41] other circuits make use of delay lines and gating circuits. Most of these will resolve pulses more than 10^{-7} second apart. Greater resolution is unnecessary if Geiger–Mueller tubes are used as detectors, since

[36] *Physical Rev.*, 1939, **55**, 321.
[37] Cooper, *ibid.*, 1942, **61**, 1.
[38] *Nature*, 1930, **125**, 636.
[39] *Z. Physik*, 1935, **95**, 419.
[40] Mandeville and Scherb, *Nucleonics*, 1948, **3**, No. 4, 2.
[41] Schultz and Pollard, *Rev. Sci. Instr.*, 1948, **19**, 617.

their response time is of the order of 10^{-6} second. With the application of the photomultiplier tubes to the detection of nuclear radiations, still greater resolution becomes desirable, because the maximum pulse is developed at the output of these tubes in rather less than 10^{-8} second. The photomultiplier tubes used, such as the E.M.I 5031, have an amplification of as much as 10^8. They can be adapted to the direct detection of α- or β-particles if the particles are allowed to impinge on the first dynode ; but, since this requires the introduction of the radioactive material within the vacuum envelope of the tube, it is usually more convenient to convert the radioactive radiation into photons of ultra-violet or blue light, by means of a material which fluoresces when exposed to radioactive radiations, and to allow the light to produce photo-electrons at the photosensitive surface of the tube.[42] In this way the necessity of introducing the radioactive material inside the tube is avoided. A wide range of fluorescent materials, both solids and solutions, has now been reported ; amongst the most satisfactory are silver-activated zinc [43] or cadmium sulphide screens or single crystals for the detection of α-particles, and anthracene [44] crystals, thallium-activated sodium iodide crystals,[45] or solutions of p-terphenyl in p-xylene [46] for the detection of β- and γ-radiations. The fluorescence of the sulphide crystals is much slower than that of the latter group of substances which respond in less than 10^{-8} second. Coincidence circuits of sufficient resolution to make use of the faster response of these detectors have already been developed. A particularly simple circuit depends on the curvature of the characteristic of a crystal diode.[47] The outputs from both photomultiplier tubes are connected to one crystal diode, and the output from the last dynode of each tube is connected through a condenser to a pair of biased diodes arranged in parallel, but with opposite polarity to the first. In this way pulses received in but one of the tubes cancel out, but coincident events produce a pulse at the common output of the three diodes because the double pulse at the output diode passes through to give a larger pulse than the sum of the pulses passed by the dynode diodes. The circuit is simple, cheap, and virtually as fast as the response of the photomultiplier tube.

The measurement of the energy spectra of the β- and γ-radiations has commanded continuous attention and has made steady progress since the earliest period of the study of radioactivity. With few exceptions, the methods of measurement of both β- and γ-energies are similar, since the latter can be deduced from the energies of the electrons produced by the interaction of the photons with the matter they traverse. Although the γ-photons are an electro-magnetic radiation and, if sufficiently low in

[42] Jordan and Bell, *Nucleonics*, 1949, **5**, No. 4, 30.

[43] Blau and Dreyfus, *Rev. Sci. Instr.*, 1945, **16**, 245.

[44] Kallmann, *Natur u. Technik*, July, 1947 ; Broser and Kallmann, *Z. Naturforsch.*, 1947, **2a**, 439.

[45] Moon, *Physical Rev.*, 1948, **73**, 1210.

[46] Kallmann, *ibid.*, 1950, **78**, 621 ; Ageno, Chiozzotto, and Querzoli, *ibid.*, 1950, **79**, 720.

[47] Baldinger, Huber, and Meyer, *Rev. Sci. Instr.*, 1948, **19**, 473.

energy, can be diffracted like X-rays at a crystal lattice, this method is seldom employed to determine their energy. More usually, their energy is deduced from that of the orbital electrons they eject by photoelectric absorption in other atoms ; or, particularly in the case of the heavy elements, the electrons emitted by internal conversion. Alternatively, their energy may be calculated from the energies of the electrons produced by Compton scattering. The latter procedure is most convenient for very energetic γ-radiation.

Before the period under review, the majority of determinations of β- and γ-ray energies were made by measurement of the absorption, or more precisely, of a combination of the absorption and the scattering of the radiation, by metal absorbers inserted between the source and the detecting device. Empirical relations between the range in matter and the maximum β-particle energy, and between the absorption coefficient and the γ-ray energy were known. However, the accuracy attainable by this method is not very great, usually not better than $\pm$ 5%, nor can superimposed β- or γ-rays of not very different energies be distinguished. Recent investigators [48] have, however, shown that by careful standardisation of the technique, some information about the form of the β-ray spectrum, as well as the maximum β-ray energies, can be obtained by these means. The precautions that must be taken to ensure reliable results with routine measurements of average accuracy have been reviewed by Glendenin.[49] A recent procedure for the rapid estimation of the maximum β-ray energy depends on measurement of their scattering alone, the " absorber " being placed behind the source.[50]

The first crude magnetic spectrograph for β-ray spectroscopy was devised by von Baeyer and Hahn [51] as early as 1910. Two years later the first semi-circular focusing magnetic spectrograph was described.[52] Instruments of this kind were used by Rutherford and his collaborators during the next decade to separate and study the nuclear β-ray spectra and the superimposed electron line spectra resulting from internal conversion of γ-radiation. This pattern of spectrograph possesses great resolving power but can only accept β-particles emitted into a very small solid angle subtended at the source ; so that large activities and long exposures are required for each measurement. Typical values are 0·4% for the resolution, with 0·15% for the geometrical efficiency. (The resolution is expressed as a percentage since it is a nearly constant fraction of the β-ray energy measured.) These properties may preclude the use of the instrument in certain cases with short-lived or weak sources. The resolution improves as the radius of the magnetic field increases, but the construction of large, very uniform magnetic fields presents considerable technical difficulties. A recently designed spectrograph [53] employs a radially non-uniform magnetic field

[48] Bleuler and Zünti, *Helv. Physica Acta*, 1946, **19**, 375.
[49] *Nucleonics*, 1948, **2**, No. 1, 12.
[50] Yaffe and Justus, *Physical Rev.*, 1948, **73**, 1400.
[51] *Physikal. Z.*, 1910, **11**, 488.
[52] Danysz, *Le Radium*, 1912, **9**, 1 ; 1913, **10**, 4.
[53] Langer and Cook, *Rev. Sci. Instr.*, 1948, **19**, 257.

in such a way as to combine high resolution with acceptance of a larger solid angle of radiation from the source than was hitherto possible.

Another method of dispersion of electrons according to their energies uses the magnetic field of a solenoid or a thin magnetic electron lens. The possibilities of such an instrument were suggested by Kapitza, and the first was designed and constructed by Tricker.[54] The source is placed at one end of a solenoid, wound to produce a longitudinal homogeneous magnetic field ; the detector is situated behind a slit at the opposite end of the solenoid. A baffle system is arranged within the solenoid such that at any determined magnetic field strength, electrons emitted by the source in a narrow band of kinetic energies are focused on the detector, after they have completed one revolution of the helical path to which they are constrained by the field. A similar instrument [55] concentrates the winding of the solenoid at its centre, forming a thin magnetic lens, such as is used in the electron microscope. The chromatic aberration of the lens results in electrons of differing initial energy reaching different focal points. Both these instruments combine a resolution of about 2% with a geometrical efficiency of about 1%. Considerable progress has been made during recent years in reconciling increased geometrical efficiency with high resolution. The problem has been studied theoretically by E. McMillan during his design studies on synchrotrons and his work has been amplified by Schull and Dennison.[56] An instrument using an inhomogeneous ring-shaped magnetic field based on similar calculations has been designed and constructed independently by Siegbahn and Svartholm.[57] With such an instrument a resolution of 0·3% can be combined with a geometrical efficiency of nearly 0·4%.

The measurement of both β- and γ-ray energies by examination of Wilson cloud-chamber photographs has been generally abandoned, except in specially favourable cases, because of the large number of photographs that must be measured to obtain reasonable statistical errors. But another method of great potential value, although not, as yet, susceptible to high resolution, has just been discovered.[43, 58] It has been shown that the maximum pulse developed in a photomultiplier tube used to record α-, β-, or γ-radiation, in conjunction with a scintillating fluorescent medium, is dependent on the energy of the exciting particles. The resolution of the method is limited by the random fluctuations in the amplification by the tube. The high sensitivity of the method permits measurement with extremely weak sources. The method is not suitable for the study of the form of β-ray spectra.

By the combination of such apparatus,[59] recording only β- or γ-rays of a

[54] *Proc. Camb. Phil. Soc.*, 1924, **22**, 454.

[55] Deutsch, Elliott, and Evans, *Rev. Sci. Instr.*, 1944, **15**, 178.

[56] *Physical Rev.*, 1947, **71**, 681 ; 1947, **72**, 256.

[57] *Nature*, 1946, **157**, 872 ; *Ark. Mat. Astr. Fys.*, 1946, **33**, *A*, 24.

[58] Kallmann and Broser, *Ann. Physik*, 1948, **4**, 61 ; Hofstadter and McIntyre, *Nucleonics*, 1950, **7**, No. 3, 32.

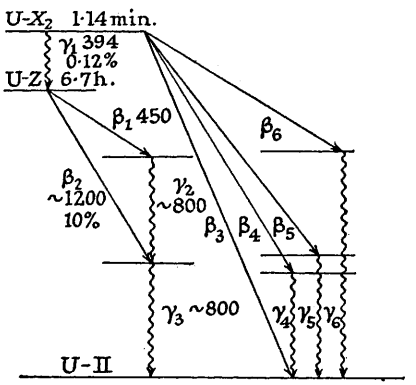
[59] See, *e.g.*, Siegbahn and Johansson, *Ark. Mat. Astr. Fys.*, 1947, **34**, *A*, 10 ; Feather, Kyles, and Pringle, *Proc. Phys. Soc.*, 1948, **61**, 466.

selected energy, with that described for the detection of very nearly coincident events, it has become possible to investigate the details of the decay mechanism of β- and γ-active species, including various nuclear isomers. Very few decay schemes, even amongst the naturally radioactive species, have yet been examined exhaustively.

The details of the U-X_2–U-Z decay schemes (annexed) were first established by Bretscher and Feather,[60] who carried out a careful absorption study. A more complete picture has been provided by the work of Bradt and Scherrer,[61] who used coincidence methods and a semicircular magnetic spectrograph.

On finding that the 394 K.e.v. γ-ray was unaccompanied by β-particle emission, that the radiation was principally internally converted in the L- and M-shells, and that in separated samples of U-X_2 and U-Z, the U-X_2 quickly decayed to leave a radiochemically pure U-Z source, it was surmised that the U-Z represents a genetically related, less energetic state of the ^{234}Pa nucleus. (The absence of K-shell internal conversion was not unexpected in view of the necessarily large spin change between the two isomers.) Measurement of the U-X_2 and U-Z activities in an equilibrium sample, together with a determination of the half-life of each, allowed the ratio of the decay probabilities of the U-X_2 for de-excitation and β-particle emission to be calculated. The other details of the decay scheme including conversion coefficients for many of the photon radiations were established by examination of the β- and γ-ray spectra of pure U-Z and the equilibrium mixture and by measurement of the ratio of coincidences between various energies of particles and photons.

U-X_2–U-Z Decay scheme

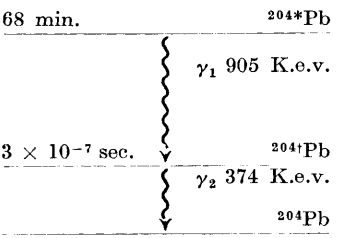


No other instances of nuclear isomerism have been detected amongst the naturally radioactive species, although a long-lived excited state of ^{230}Th has been suggested by Feather,[62] who has also pointed out that the reported branching by Th-A (see p. 282) would imply a long-lived isomer of Th-C. Mattauch [63] has advanced two empirical rules concerning the occurrence of isomers of stable nuclei. He points out that nuclei containing even numbers of both protons and neutrons do not give rise to isomers, whereas all nuclei with ground states of spin 9/2 or greater appear to possess a metastable state. These rules are plausible since even-even nuclei have ground states of zero spin and the first excited level commonly lies at about 1 M.e.v. and is therefore too high for the existence of a long-lived excited state ; whereas nuclei of spin 9/2 must commonly possess low-lying excited

[60] *Proc. Roy. Soc.*, 1938, *A*, **165**, 530.
[61] *Helv. Physica Acta*, 1945, **18**, 405.
[62] *Nucleonics*, 1949, **5**, No. 1, 22.
[63] *Z. Physik*, 1941, **117**, 246.

states of spin 3/2 or 1/2 which might be expected to be long-lived. With the exception of the 43-min. ^{199}*Hg no other nuclear isomers [66] have been reported in the $4n + 3$ series amongst either its natural or synthetic members although it is possible that isomers of Rd-Ac and Ac-*X* might exist.

Of the synthetic nuclei of the remaining series, the tables show two pairs of isomers [64] in the $4n$ series, ^{204}*Pb and ^{208}*At ; three pairs in the [65] $4n + 1$ series, ^{201}*Bi, ^{197}*Hg, and ^{201}*Hg ; while the $4n + 2$ series [67] possesses two examples ^{242}*Am and ^{210}*Bi. Of these, ^{204}*Pb is much the most remarkable since the pair constitutes one of the two recorded exceptions to Mattauch's rules. A close examination [68] of the decay of the excited species has revealed further interesting detail. The first photon emission gives rise to a second long-lived, although more transient state which emits a second photon to produce the ground state.



It seems probable that both the excited and the ground states have zero spin, zero-zero transitions being strongly forbidden. Decay can only take place *via* an intermediate state of large integral spin, and both transitions may be expected to be long-lived.[33] The total excitation energy of the 68-min. isomer is unusually high for nuclear isomerism, but this is not, perhaps, unexpected in such a case. Both photons are weakly converted in the *K*- and *L*-shells.

For some of these isomeric pairs the further mode of α-emission may be possible. Naturally, the isomers differ in α-decay characteristics ; thus in the case of the ^{242}Am pair only the longer-lived isomer is α-active although α-emission may constitute a very rare mode of decay of the other isomer. In the case of the ^{208}At isomers only the shorter-lived member has been observed to be α-active. Only ^{234}*Pa, ^{204}*Pb, and ^{201}*Hg isomers belong to the genetically related group of isomers ; [33] the others behave like independent isotopes with individual radiation characteristics.

Branching in the Natural Decay Series.—At the time of the discovery of artificial radioactivity the only nuclei definitely known to disintegrate by competitive processes were the *C*-members of each series which gave rise to the *C'*-members by β-emission and to the *C''*-members by α-emission. Several other instances of branch modes of decay are now established.

[64] Fajans and Voigt, *Physical Rev.*, 1941, **60**, 619 ; Hyde, Ghiorso, and Seaborg, *ibid.*, 1950, **77**, 765 ; Barton, Ghiorso, and Perlman, see Nat. Bur. Stand. Circ. 499.

[65] Neumann and Perlman, *Physical Rev.*, 1950, **78**, 191 ; Huber, Steffen, and Humbel, *Helv. Physica Acta*, 1948, **21**, 192.

[66] Friedlander and Wu, *Physical Rev.*, 1943, **63**, 227.

[67] Seaborg, James, and Morgan, National Nuclear Energy Series, Div. IV, Vol. 14B (McGraw-Hill, 1949, N.Y.), Paper 22.1 ; Neumann, Howland, and Perlman, U.S. Atomic Energy Commission, U.C.R.L. 561, Declassified Dec. 1949.

[68] Sunyar, Alburger, Friedlander, Goldhaber, and Scharff-Goldhaber, *Physical Rev.*, 1950, **78**, 326.

Francium.—The α-activity of actinium was reported as long ago as 1913,[69] but the rarity and difficulty of preparing strong sources of actinium, and the problems attending the identification of the actinium activity in the inevitable presence of its strongly α-active decay products, delayed further study of the subject for nearly a quarter of a century. Nor was an attempt made in the intervening years to isolate the product of this mode of decay.

In 1938, Schintlmeister [70] predicted that both actinium and mesothorium-II might be expected to be weakly α-active. He drew these conclusions from a study of the stability surfaces derived from the decay energies of the surrounding nuclei. It appeared that the half-life to be expected for the α-activity of the actinium was such that it should easily be detected competing with the normal decay of the actinium. In the following year, Perey [71] succeeded in identifying the α-activity, separating and characterising the daughter body, then called actinium-*K*. This short-lived, natural isotope of element 87 has a half-life of 20 minutes and decays by the emission of β-particles of maximum energy 1·1 M.e.v., accompanied by γ-rays of 95 K.e.v.[72] The latter radiation is strongly converted in the *L* shell. Element 87 has subsequently been given the name francium by Perey,[73] so that actinium-*K* is ^{223}Fr.

By means of this isotope, which is still the longest-lived known isotope of francium, the chemistry of the element has been studied by using tracer methods. The element is the heaviest alkali metal and, as might be predicted, possesses very few characteristic co-deposition reactions; but it can be separated from other elements, cæsium or rubidium being used as carrier, on the perchlorate, picrate, or phosphotungstate after removal of most other metals by the addition of sodium hydroxide and carbonate. Since nearly all francium salts are soluble and because its radiation characteristics are distinctive, the separation and estimation of the actinium-*K* has been proposed as a method of assaying actinium.

A claim [74] that mesothorium-II was also α-active dates from about the same time as the first observation on the α-activity of actinium. Recently, Guében [75] has confirmed these observations. Further theoretical consideration [70] of the α-energy suggests too low a branching ratio to permit detection, and further investigation [76] has not substantiated Guében's claim. The existence of any long-lived, or indeed, of any other naturally occurring isotopes of francium now seems most improbable.

It has been predicted that actinium-*K* should also exhibit α–β branching with a ratio of a few per thousand disintegrations, but this weak α-activity,

[69] Hahn and Rothenbach, *Physikal. Z.*, 1913, **14,** 409; Meyer, Hess, and Paneth, *Ber. Akad. Wiss. Wien,* 1914, Abt. 2*a*, **123,** 1459.

[70] *Österr. Chem.-Ztg.*, 1938, **41,** 315; Jenschke, *Physical Rev.*, 1950, **77,** 98.

[71] *Compt. rend.*, 1939, **208,** 97; *J. Phys. Radium,* 1939, **10,** 435.

[72] Lecoin, Perey, and Teillac, *ibid.*, 1949, **10,** 33.

[73] See Paneth, *Nature,* 1947, **159,** 8.

[74] Cranston, *Phil. Mag.*, 1913, **25,** 712.

[75] *Ann. Soc. sci. Brux.*, 1933, **53,** 115.

[76] Rona and Schintlmeister, *Ber. Akad. Wiss. Wien,* 1938, Abt. 2*a*, **147,** 49.

which should give rise to the still unknown isotope ^{219}At, has not been detected.[77]

Astatine.—The record of the study of the β-activity of the A-products of the natural decay series is now quite extensive, but only one of the three cases seems fairly established.

Although β-branching by radium-A was predicted in 1940,[78] and in the same year Minder [79] claimed to have detected such a mode of decay, these observations were soon shown to be erroneous.[80] But three years later, Karlik and Bernert [81] demonstrated the production of an α-active daughter, ^{218}At, from the β-decay of radium-A.

The branching ratio of the $\alpha : \beta$ modes of decay was shown [82] to be $10^4 : 3{\cdot}3$, but the actual β-activity of the radium-A has not yet been detected. Since ^{218}At has not been prepared artificially, the possibility of some other explanation of these observations cannot be excluded. Essentially similar results were obtained by Walen,[83] who found that the ^{218}At also exhibited branching. The latter investigator gives 1·5—2·0 seconds as the half-life of ^{218}At and confirms the earlier value of 6·63 M.e.v. for the energy of its α-particles. However, he finds that ^{218}Rn, the product of the β-decay of the ^{218}At, has a half-life of 1·3 seconds, whereas Studier and Hyde find a value of 0·02 second for the synthetic ^{218}Rn nuclei.[84]

Although the β-particles emitted by the Ra-A have not been detected, one can calculate their maximum energy [77, 82] by equating the energies lost in passing from Ra-A to Ra-C by the two alternative routes. The calculation assumes that both routes lead to the same isomeric state of Ra-C. Now the α-particle energy of 6·63 M.e.v. found for the ^{218}At radiation leads to a disintegration energy of 6·75 M.e.v. after allowance for the recoil of the heavy nucleus. Similarly, the disintegration energy for α-emission by Ra-A is 6·09 M.e.v., and the energy released in the emission of the β- and γ-rays by the Ra-B nucleus is 0·96 M.e.v. Therefore the maximum β-ray energy from the Ra-A must be 0·3 M.e.v. Such a value is theoretically compatible with the observed branching ratio and an allowed β-transition.

The β-branching of thorium-A now begins to appear somewhat improbable. The first report [85] was based on the supposed separation of an α-active material from the thoron-active deposit by volatilisation at so low a temperature that it was believed only astatine might be separated. Repetition of the experiments under more stringent conditions was unsuccessful, but the same investigators detected an α-active body emitting particles of 7·58 M.e.v., present in the thoron decay products to the extent of 1·35

[77] Vigneron, *Compt. rend.*, 1947, **225**, 1067 ; Feather, Brit. Atomic Energy Rep., Br. 640 (1945).

[78] Turner, *Physical Rev.*, 1940, **57**, 950. [79] *Helv. Physica Acta*, 1940, **13**, 144.

[80] Karlik and Bernert, *Ber. Akad. Wiss. Wien*, 1942, Abt. 2*a*, **151**, 255.

[81] *Naturwiss.*, 1943, **31**, 298. [82] Karlik and Bernert, *Z. Physik*, 1944, **123**, 51.

[83] *Compt. rend.*, 1948, **227**, 1090 ; *J. Phys. Radium*, 1949, **10**, 95.

[84] *Physical Rev.*, 1948, **74**, 591 ; Studier, U.S. Atomic Energy Commission, A.E.C.D. 2445, Declassified Jan. 1949.

[85] Leigh-Smith and Minder, *Nature*, 1942, **150**, 767.

disintegrations for each 10^4 disintegrations of Th-*A*.[82] They attributed this activity to ^{216}At formed by the β-decay of Th-*A*. The same isotope has recently been prepared synthetically [86] but the product so obtained emits α-particles of 7·79 M.e.v. The difference between the two values is much greater than the possible experimental error of the measurements. A more serious difficulty [77, 82, 87] arises from the energy balance between the two routes from Th-*A* to Th-*C*. The α-disintegration energy of Th-*A* is 6·90 M.e.v., and the energy released by the β-decay of Th-*B* is 0·57 M.e.v. Thus, without making allowance for the β-energy of Th-*A* decay, the energy emitted along the Th-*B* branch is less than that for the ^{216}At branch whichever value for the ^{216}At α-decay energy be used. A reasonable assumption as to the Th-*A* β-energy leads to an energy difference of about 1 M.e.v. between the two paths.

Two explanations of these observations have been advanced, both involving hypothetical nuclear isomers. Flugge and Krebs [87] accept the β-branching by the Th-*A* but suggest that the normal 60·5-min. Th-*C* is an excited nuclear isomer. The ground state of Th-*C* is only formed by the ^{216}At route. Its nuclear properties are unknown, but it might be expected to be longer-lived than the common form. On the other hand, Feather [77] points out that the β-branching hypothesis is superfluous. The energetic α-particles, which constitute the sole experimental evidence may arise from the decay of an excited isomer of Th-*A*. This hypothesis implies a fine structure for the thoron α-spectrum. Each hypothesis can readily be tested experimentally but no such study has yet been reported.

Karlik and Bernert also reported [82] the detection of a small group of long-ranged α-particles emitted by actinon and its decay products with an intensity corresponding to a β/α branching ratio of $2 : 10^6$. The α-particle energy corresponded to about 8·4 M.e.v. They suggested that these particles were emitted from ^{215}At formed by the β-branching of Ac-*A* ; but they observed that their value of $5 : 10^6$ for the branching ratio would require a β-disintegration energy of about 1·5 M.e.v., so that the energy deficit along the main Ac-*A*–Ac-*B*–Ac-*C* decay chain would amount to about 1 M.e.v. The α-particles from synthetic ^{215}At have been shown [88] to be of 8·0 M.e.v. These observations present similar difficulties to those discussed with Th-*A*. A similar pair of *ad hoc* hypotheses can be advanced, but until more detailed experimental evidence is reported, the question of the β-branching of both Th-*A* and Ac-*A* must be regarded as open.

In each case the astatine isotopes are too short-lived for chemical investigation and the study of this element has been conducted exclusively with synthetic isotopes (see p. 296).

The Branching at Ra-*E*.—Radium-*E* has been shown [89] to decay by α-particle emission with a branching ratio of about $3 : 10^7$. The product of this mode of decay, Ra-*E*′ (^{206}Tl) has been proved to be the 4·2-min.

[86] Ghiorso, Meinke, and Seaborg, *Physical Rev.*, 1948, **74**, 695.
[87] *Naturwiss.*, 1944, **32**, 71.
[88] Meinke, Ghiorso, and Seaborg, *Physical Rev.*, 1949, **75**, 314.
[89] Broda and Feather, *Proc. Roy. Soc.*, 1947, *A*, **190**, 20.

β-active thallium isotope, thus changing the earlier isotopic allocation of ^{204}Tl to ^{206}Tl. The Ra-E' was separated by means of the mechanical recoil suffered by the nucleus emitting an α-particle.

Developments in the Measurement of Radioactivity.—The period covered by this Review has seen a profound change in the methods of measurement of radioactivity, particularly in the estimation of α-active substances. These improvements have greatly facilitated advances in our knowledge of the radioactivity of the heavy elements. Although the Geiger tube was known [90] as early as 1908, the more convenient self-quenching Geiger–Mueller tube was not discovered [91] till 1928. Until this time, measurements were generally made with ionisation chambers in conjunction with electroscopes, but within a few years the Geiger–Mueller tube was almost universally employed for the measurement of β-activity and to a considerable extent for the estimation of γ-active substances. Such is still the position, although alternative procedures are now finding greater favour. The scintillation counter, whose sensitivity to γ-radiation exceeds that of any Geiger–Mueller tube, has already been described. Besides, the full value of the proportional counter is now more widely appreciated. Current practice in electronic circuit design for radioactive measuring instruments has recently been reviewed by Scarrot.[92]

The Geiger–Mueller tube records each ionising event as a small-voltage pulse which reaches its maximum size in a few microseconds and decays in some ten times this period. These pulses may either be recorded individually by means of a scaler, or the mean rate of production can be determined. The first application of electronic methods, as distinct from mechanical or electro-mechanical methods, to the problem of counting such pulses was made by Wynn-Williams.[93] He devised a circuit that would only produce an output pulse for every second input pulse and whose momentary condition was readily distinguished. By combining one, two, three, or four such units in series, scalers recording in the scales of 2, 4, 8, or 16 can be constructed. The fundamental scale-of-2 circuit has undergone considerable modification, and methods of combination have been described which enable decade scalers to be constructed.[94] The resolving time of these scalers has been reduced progressively so that random counting is now possible at as great a rate as 50,000 counts/sec., with less than 1% loss due to coincidences. A recent development suggests that it may be possible to produce a single valve capable of functioning as a decade scaler.[94]

Alternatively, the pulses can be made to trigger an equalising stage such that each pulse is brought to a common size. These uniform pulses are fed to an integrating circuit which produces a voltage proportional to the mean rate of arrival of the primary pulses. Several circuits fulfilling

[90] Rutherford and Geiger, *Proc. Roy. Soc.*, 1908, *A*, **81**, 141.

[91] Geiger and Mueller, *Physikal. Z.*, 1928, **29**, 839.

[92] Progress in Nuclear Physics (Editor O. R. Frisch), Butterworth-Springer, London, 1950.

[93] *Proc. Roy. Soc.*, 1931, *A*, **132**, 295, 312.

[94] Regener, *Rev. Sci. Instr.*, 1946, **17**, 375; Rotblat, Sayle, and Thomas, *J. Sci. Instr.*, 1948, **25**, 33; Bacon and Pollard, *Elec. Eng.*, 1950, **22**, 173.

this function have been designed. The instrument is called a counting rate meter.[95]

If a non-quenching Geiger tube is operated at a collecting potential considerably below the Geiger region, each ionising event produces a pulse proportional to the primary ionisation produced in the tube. The operation of the proportional counter was well known before the discovery of the Geiger–Mueller tube. Its value in distinguishing between γ-rays, β- and α-particles by the difference in the specific ionisation produced in the tube was also established.[96] However, the use of proportional counters was not widespread. More recently, their advantages in the measurement of very soft β-radiations have been exploited.[97] Most are possessed by the continuous-flow proportional counters. With these the sample is introduced within the tube through a gas-tight sleeve. Connections are arranged for continuously flushing the tube with methane gas. The device possesses three advantages : the absence of a window separating the sample from the sensitive part of the counter, the fast response of the counter, which permits a greater counting rate than is possible with a Geiger–Mueller tube, and, finally, the possibility of measuring small β-activities in the presence of a much greater γ-activity.

The proportional counter has also been applied to the study of soft β-ray spectra. By the application of a longitudinal magnetic field to the counter the electrons released from a radioactive gaseous filling are constrained to dissipate the whole of their energy within the counter.[98] In this way the output pulses become directly proportional to the energy of the initiating β-particles. Proportional counters have been described which enable the pulses from an ionising event releasing but 50 ion pairs to be distinguished above the background.[99]

More radical changes have attended the measurement of α-activity. It is therefore the more curious to find the most recent developments involve a return to the principles of the earliest method. In these investigations individual α-particles were counted subjectively by direct observation of the flashes of light they produced by impact with a zinc sulphide screen. Nevertheless, electronic amplification of the individual pulses produced by the α-particles in an ionisation chamber, to a size capable of actuating an electromechanical register was successfully accomplished by Greinacher as long ago as 1926.[100] The stages of the linear amplifier he used were transformer coupled. It was also shown possible to detect the pulses from the ionisation chamber by means of a binant electrometer.[101] Alternatively,

[95] Kip, Bousquet, Evans, and Tuttle, *Rev. Sci. Instr.*, 1946, **17**, 323 ; Bousquet, *Nucleonics*, 1949, **4**, No. 2, 67.

[96] May, *Rep. Prog. Physics*, 1938, **5**, 390 ; Lewis, Nat. Res. Coun. Canada, Report D.L.-2, June (1949).

[97] Thomas and Underwood, *Rev. Sci. Instr.*, 1948, **19**, 637 ; Bernstein and Ballentine, *ibid.*, 1949, **20**, 347.

[98] Curran, Angus, and Cockcroft, *Nature*, 1948, **162**, 302 ; Angus, Cockcroft, and Curran, *Phil. Mag.*, 1949, **40**, 522.

[99] Kirkwood, Pontecorvo, and Hanna, *Physical Rev.*, 1948, **74**, 497 ; Curran, Angus, and Cockcroft, *Phil. Mag.*, 1949, **40**, 36.

[100] *Z. Physik*, 1926, **36**, 364.

[101] Ziegert, *ibid.*, 1927, **46**, 668.

α-particles had been recorded by Geiger tubes fitted with very thin windows. But the developments in electronic technique in the years preceding the discovery of artificial radioactivity stimulated the construction of resistance-capacity coupled linear amplifiers of suitable frequency response and amplification to operate scalers or other devices, from input pulses from an ionisation chamber.[102]

Two kinds of ionisation chamber must be distinguished. Air-filled parallel-plate ionisation chambers are commonly used in radioactivity for the estimation of α-active substances. They possess very marked disadvantages. The electrons released by the passage of the α-particle are extensively captured by molecules of the air in the chamber with the production of heavy negative ions. For this reason the voltage pulse develops rather slowly, the collection time is prolonged, and a large collecting potential must be applied. The overall pulse length may be as much as 1 millisecond and the chamber cannot be operated at high counting rates without encountering large coincidence losses. The amplifier must respond at quite low frequencies to deal with such pulses. As a result the apparatus becomes very liable to microphonic disturbance. This form of apparatus was widely employed in the United States Manhattan project.[103]

If, however, the chamber is made gas-tight and filled with a mixture of argon and a trace of carbon dioxide the formation of heavy negative ions is avoided and the pulse produced is very sharp. The upper frequency limit for the amplifier has to be increased to about 2 M.c. The collecting potential need not be more than a hundred volts and the apparatus is no longer microphonic. In either case, if the ionisation chamber is designed [104] so that the α-particles expend all their energy within the sensitive volume of the chamber, the output pulses are proportional to the energy of the initiating particles.

The continuous-flow proportional counter has also found favour for the measurement of α-activity,[105] particularly in the presence of large β-activities, but the most recently adopted method returns to the scintillations produced by the α-particles on hitting a zinc sulphide or similar screen.[106] The scintillations are recorded electronically by means of a photo-multiplier tube. The method is especially suitable to the measurement of very low α-activities, since the background, or activity recorded by the apparatus in the absence of a sample, can easily be reduced to a few counts per hour.[107]

Although electronic methods have appeared pre-eminent during the last decade the development of the electrometer has not been neglected. The Lindemann quartz fibre electrometer found widespread application to the measurement of the α-, β-, and γ-radiations, but it has now been

[102] Waddel, *Rev. Sci. Instr.*, 1939, **10**, 311.

[103] Hood, U.S. Atomic Energy Commission, A.E.C.D. 2535, 2536, Declassified Oct. 1948.

[104] Rossi and Staub, National Nuclear Energy Series, Div. V, Vol. 2 (McGraw-Hill, 1949, N.Y.).

[105] Simpson, *Rev. Sci. Instr.*, 1947, **18**, 884.

[106] Graves and Dyson, *ibid.*, 1949, **20**, 560.

[107] Reed, *Nucleonics*, 1950, **7**, No. 6, 56.

improved upon by modifications specially designed with reference to the radiation and ionisation chamber with which they are used. The Lauritsen electroscope [108] is an example of such an instrument. A range of particularly sensitive, yet robust and versatile electroscopes and associated ionisation chambers have been designed and constructed by Carmichael and his collaborators in the Atomic Energy Division of the National Research Council, Chalk River, Canada.[109]

Synthetic Radioactive Heavy Nuclei

Explanatory Note about Diagrams.—The natural decay chains are shown in heavily lined boxes, the origin of each chain being enclosed in a circle. Hatched boxes correspond to stable nuclei; the others contain the half-life of the unstable species.

By plotting, I–Z isobaric nuclei lie along diagonals, which are extended as dotted lines ending at the mass number. α-Particle emission is indicated by a horizontal line between boxes. A diagonal arrow pointing downwards and to the right of the table indicates β-decay; an arrow in the opposite direction denotes orbital-electron capture. Broken lines are used where expected disintegration processes have not so far been detected. The maximum α-particle energy reported is shown above the line denoting the transition. Branching percentages are shown in square brackets if alternative modes of disintegration have been observed. (Sources of the data are given in National Bureau of Standards Circ. No. 499; see also ref. 205.)

Developments preceding the Discovery of Fission.—The effects of the neutron irradiation of the more readily procurable long-lived or stable heavy elements were studied soon after the discovery of artificial radioactivity. A preliminary survey was made by Amaldi, d'Agostino, Fermi, Rasetti, and Segrè.[110] They described radioactive products from the radiative capture of thermal neutrons (n,γ reaction) in thallium, thorium, and uranium but found no effect upon mercury, lead, or bismuth. Subsequent investigators confirmed that the last two elements had, at the most, very small capture cross-sections for thermal neutrons.[111] More detailed experiments with mercury led to the identification [112] of ^{197}Hg. Thallium was shown to give two activities, but it was not possible to determine which was due to the ^{204}Tl and which to the ^{206}Tl isotope.[113] Both thorium and uranium gave rise to a complex mixture of activities,[114] but detailed analysis was not possible until the nature of the fission process was recognised. However, the production of ^{233}Th from thorium and the identity and properties of its decay product ^{233}Pa were established.[115]

[108] C. C. Lauritsen and T. Lauritsen, *Rev. Sci. Instr.*, 1937, **8**, 438.

[109] See Nat. Res. Coun. Review, 1950 (Canada), p. 180.

[110] *Ric. Sci.*, 1934, **2**, 21. [111] Preiswerk and Halban, *Compt. rend.*, 1935, **201**, 722.

[112] Anderson, *Nature*, 1936, **137**, 457.

[113] McLennan, Grimmett, and Read, *ibid.*, 1935, **135**, 505.

[114] Fermi, Amaldi, d'Agostino, Rasetti, and E. Segrè, *Proc. Roy. Soc.*, 1934, *A*, **146**, 483.

[115] Hahn and Meitner, *Naturwiss.*, 1935, **23**, 310; Meitner, Strassmann, and Hahn, *Z. Physik*, 1938, **109**, 538; Grosse, Booth, and Dunning, *Physical Rev.*, 1941, **59**, 322; Seaborg, Gofman, and Kennedy, *ibid.*, p. 321.

All the above nuclei were produced by the radiative capture of thermal neutrons but some few products of fast neutron irradiations, produced by the $(n,2n)$ and the (n,n) reactions, were detected. The 43-minute nuclear isomer of ^{199}Hg was obtained by the fast-neutron irradiation of mercury,[116] but the isotopic identification of the activity was not made till some years later. Uranium-Y was produced [117] by the irradiation of thorium ($n,2n$ reaction) and the 68-minute nuclear isomer of lead was produced by the (n,n) reaction on lead.[118] Somewhat later, ^{203}Pb and ^{237}U were discovered amongst the products of the fast-neutron irradiation of lead [120] and uranium,[119] respectively.

Relatively few charged particle reactions with the heavy nuclei were studied before the discovery of fission. During this period the most powerful particle accelerator in the world was the Berkeley 37″ cyclotron.[121] This instrument commenced operation in 1933, at which time it was equipped with a $27\frac{1}{2}$″ magnet, but it was adapted to a 37″ magnet a few years later. This cyclotron could accelerate deuterons [122] to some 6 or 7 M.e.v. Since the Coulomb barrier for the heavy nuclei amounts to some 15 M.e.v. the cross-section for reactions with charged bombarding particles will not be very large unless their energies approach this value. Therefore the most energetic particles available were insufficient to effect nuclear transformations with good yields in this mass region. One exception must be noted : it had been shown that the (d,p) reaction exhibited a very different relation between its cross-section and the deuteron energy ; thus it could be detected at much lower energies than alternative reactions with charged particles. The deuteron is polarised by the nuclear field so that the neutron can enter the nucleus without the associated proton having to penetrate the Coulomb barrier. The reaction leads to the same product as radiative thermal neutron capture.[123]

By means of this reaction ^{209}Pb and Ra-E were produced from lead [124] and bismuth,[125] respectively. The production of Ra-E by radiative thermal neutron capture by bismuth was not discovered until later.[127] ^{197}Hg was also prepared by the deuteron bombardment of mercury.[116]

By 1939 two or three cyclotrons, capable of accelerating deuterons to the requisite energy, had begun to operate and by the middle of the year the new 60″ cyclotron at Berkeley began working.[126] In this and the

[116] Heyn, *Nature*, 1937, **139**, 842 ; McMillan, Kamen, and Ruben, *Physical Rev.*, 1937, **52**, 375.

[117] Nishina, Yasaki, Kimura, and Ikawa, *Nature*, 1938, **142**, 874.

[118] de Vries and Diemer, *Physica*, 1939, **6**, 599 ; Templeton, Howland, and Perlman, *Physical Rev.*, 1947, **72**, 766.

[119] Nishina, Yasaki, Ezoe, Kimura, and Ikawa, *ibid.*, 1940, **57**, 1182.

[120] Fajans and Voigt, *ibid.*, 1940, **58**, 177.

[121] Laurence and Livingston, *ibid.*, 1934, **45**, 608. [122] *Idem*, *ibid.*, 1936, **50**, 1131.

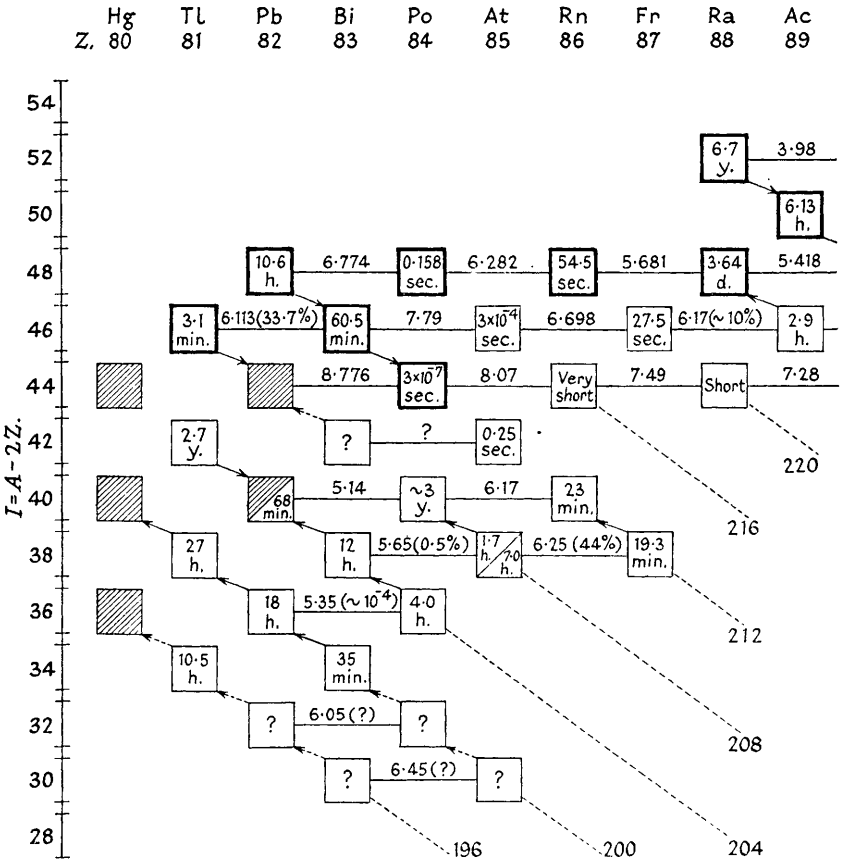
[123] Oppenheimer and Phillips, *ibid.*, 1935, **48**, 500.

[124] Thornton and Cork, *ibid.*, 1937, **51**, 383.

[125] Livingood, *ibid.*, 1936, **50**, 425.

[126] Laurence and Livingston, *ibid.*, 1939, **56**, 124.

[127] Maurer and Ramm, *Z. Physik*, 1942, **119**, 602 ; Goldhaber and Goldhaber, *Physical Rev.*, 1941, **59**, 102.


Hg Tl Pb Bi Po At Rn Fr Ra Ac
Z. 80 81 82 83 84 85 86 87 88 89
I=A-2Z.
54
52
50
48
46
44
42
40
38
36
34
32
30
28
6·7 y.
3·98
6·13 h.
10·6 h.
6·774
0·158 sec.
6·282
54·5 sec.
5·681
3·64 d.
5·418
3·1 min.
6·113(33·7%)
60·5 min.
7·79
3×10⁻⁴ sec.
6·698
27·5 sec.
6·17(~10%)
2·9 h.
8·776
3×10⁻⁷ sec.
8·07
Very short
7·49
Short
7·28
220
2·7 y.
?
?
0·25 sec.
216
68 min.
5·14
~3 y.
6·17
23 min.
27 h.
12 h.
5·65(0·5%)
1·7 h. / 7·0 h.
6·25 (44%)
19·3 min.
212
18 h.
5·35 (~10⁻⁴)
4·0 h.
208
10·5 h.
35 min.
6·05(?)
?
?
6·45(?)
?
196
200
204

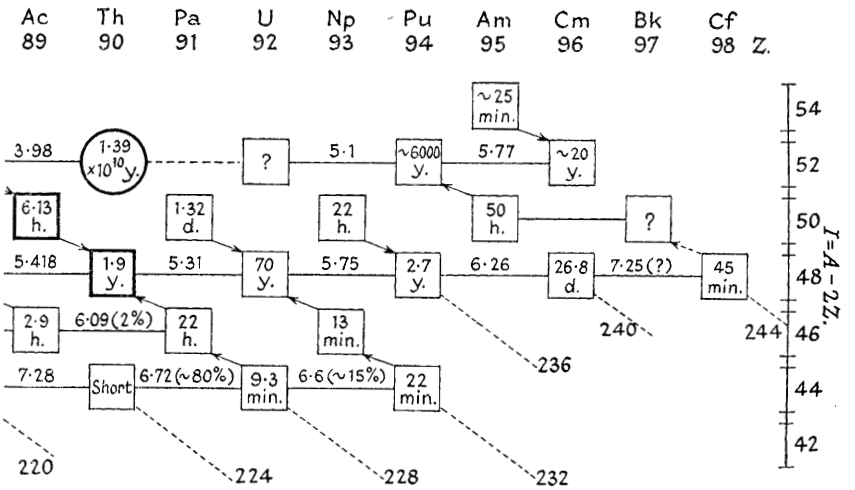
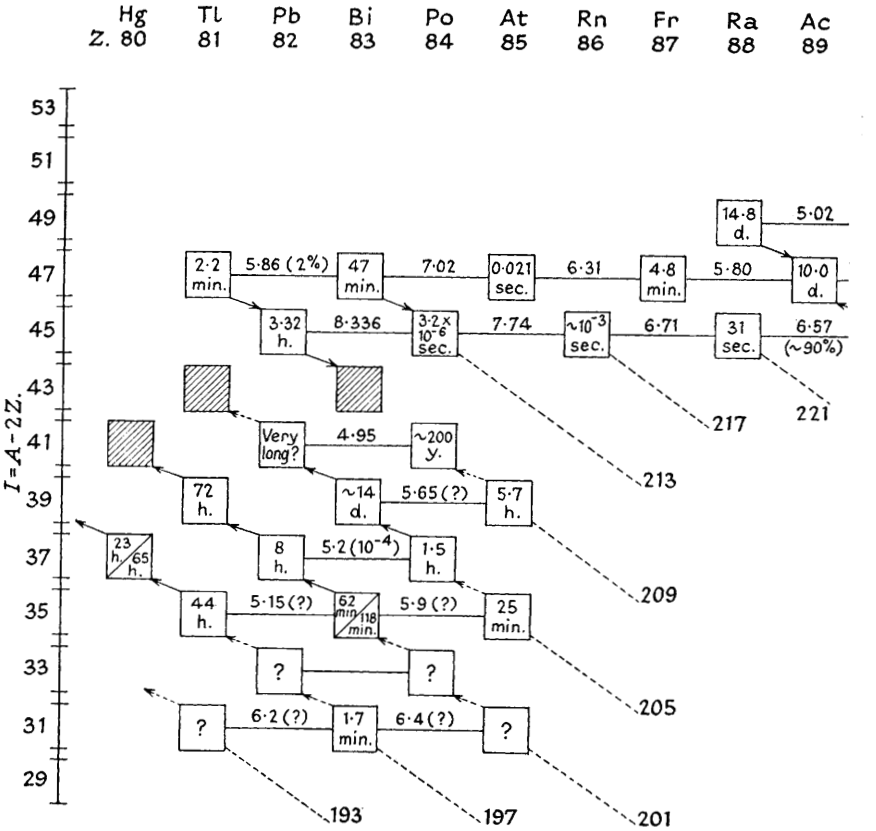


FIG. 1.—*4n* SERIES.


Hg Tl Pb Bi Po At Rn Fr Ra Ac
Z. 80 81 82 83 84 85 86 87 88 89
I=A-2Z.
53
51
49
47
45
43
41
39
37
35
33
31
29
2·2 min.
5·86 (2%)
47 min.
7·02
0·021 sec.
6·31
4·8 min.
5·80
10·0 d.
14·8 d.
5·02
3·32 h.
8·336
3·2×10⁻⁶ sec.
7·74
~10⁻³ sec.
6·71
31 sec.
6·57 (~90%)
Very long?
4·95
~200 y.
72 h.
~14 d.
5·65 (?)
5·7 h.
23 h. / 65 h.
8 h.
5·2 (10⁻⁴)
1·5 h.
44 h.
5·15 (?)
62 min / 118 min.
5·9 (?)
25 min.
?
?
?
6·2 (?)
1·7 min.
6·4 (?)
?
193
197
201
205
209
213
217
221

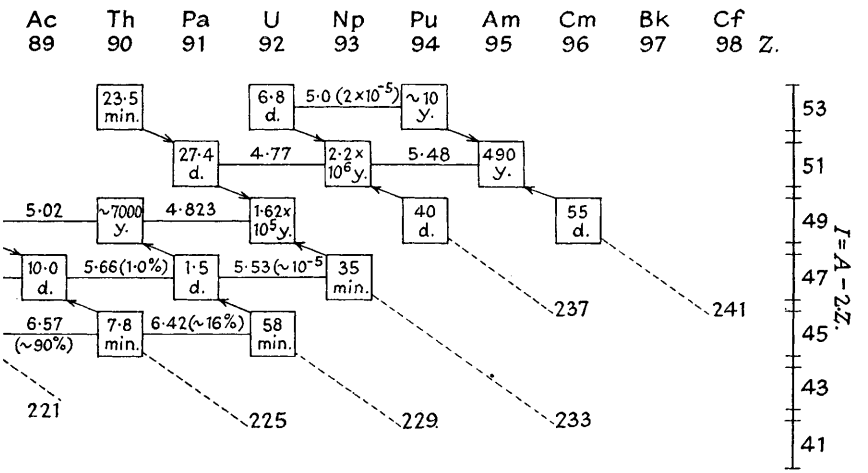
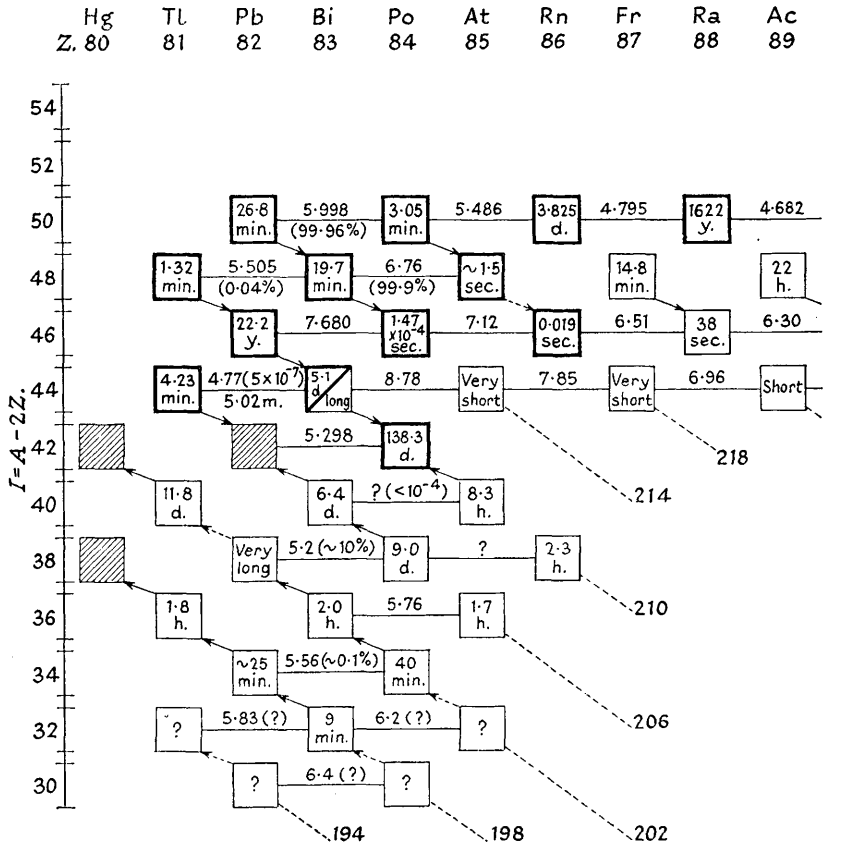
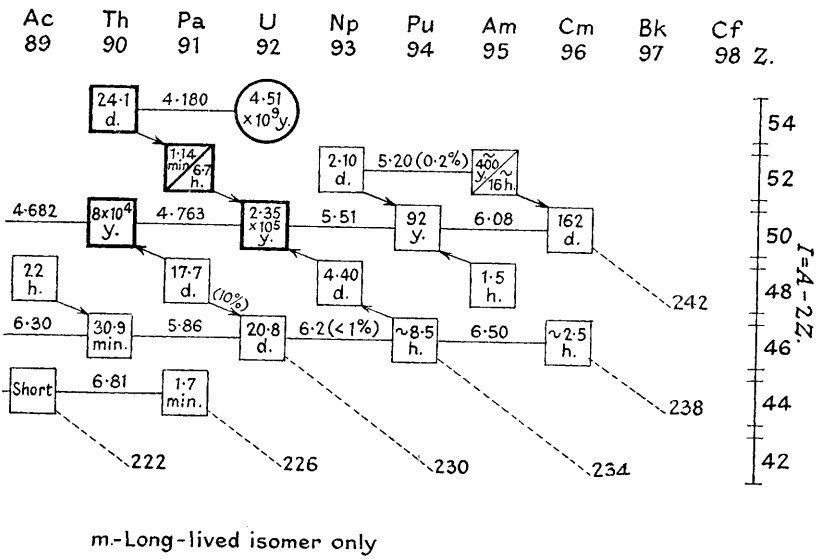


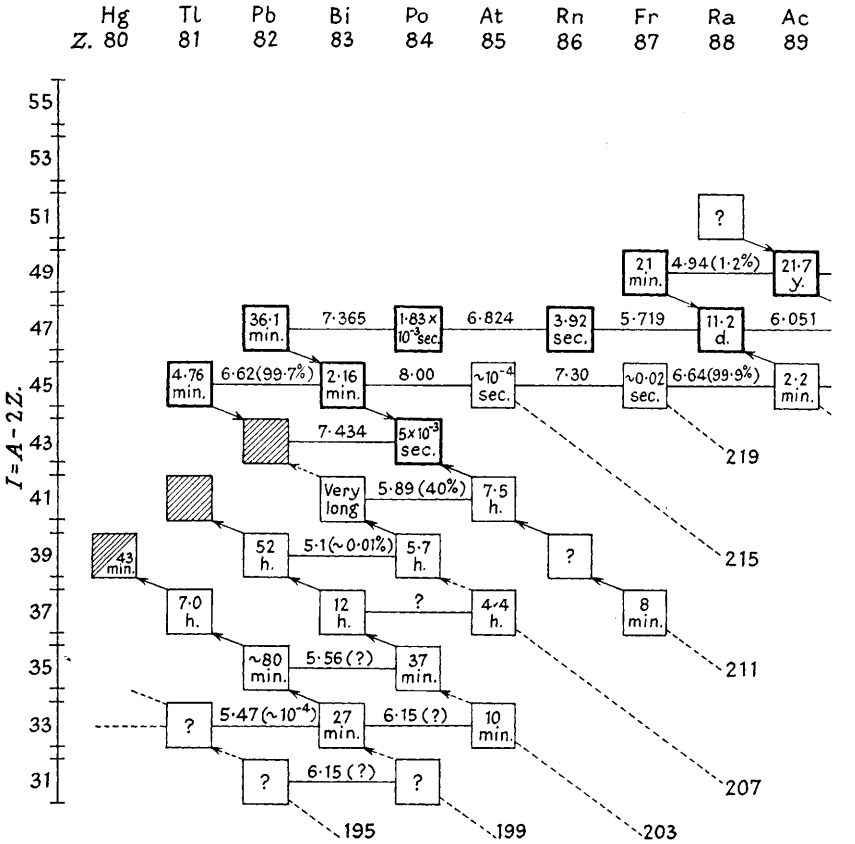
FIG. 2.—$4n + 1$ SERIES.


Hg Tl Pb Bi Po At Rn Fr Ra Ac
Z, 80 81 82 83 84 85 86 87 88 89
I = A − 2Z.
54
52
50
48
46
44
42
40
38
36
34
32
30
26·8 min.
5·998 (99·96%)
3·05 min.
5·486
3·825 d.
4·795
1622 y.
4·682
1·32 min.
5·505 (0·04%)
19·7 min.
6·76 (99·9%)
~1·5 sec.
14·8 min.
22 h.
22·2 y.
7·680
1·47 ×10⁻⁴ sec.
7·12
0·019 sec.
6·51
38 sec.
6·30
4·23 min.
4·77(5×10⁻⁷)
5·02m.
5·1 α long
8·78
Very short
7·85
Very short
6·96
Short
5·298
138·3 d.
218
214
11·8 d.
6·4 d.
? (<10⁻⁴)
8·3 h.
Very long
5·2 (~10%)
9·0 d.
?
2·3 h.
210
1·8 h.
2·0 h.
5·76
1·7 h.
~25 min.
5·56(~0·1%)
40 min.
206
?
5·83 (?)
9 min.
6·2 (?)
?
?
6·4 (?)
?
194
198
202



m.-Long-lived isomer only

FIG. 3.—$4n + 2$ SERIES.


Hg Tl Pb Bi Po At Rn Fr Ra Ac
Z. 80 81 82 83 84 85 86 87 88 89
I=A-2Z.
55
53
51
49
47
45
43
41
39
37
35
33
31
?
21 min.
4·94 (1·2%)
21·7 y.
36·1 min.
7·365
1·83 × 10⁻³ sec.
6·824
3·92 sec.
5·719
11·2 d.
6·051
4·76 min.
6·62 (99·7%)
2·16 min.
8·00
~10⁻⁴ sec.
7·30
~0·02 sec.
6·64 (99·8%)
2·2 min.
7·434
5×10⁻³ sec.
219
Very long
5·89 (40%)
7·5 h.
215
43 min.
52 h.
5·1 (~0·01%)
5·7 h.
?
7·0 h.
12 h.
?
4·4 h.
8 min.
211
~80 min.
5·56 (?)
37 min.
5·47 (~10⁻⁴)
27 min.
6·15 (?)
10 min.
207
6·15 (?)
195
199
203

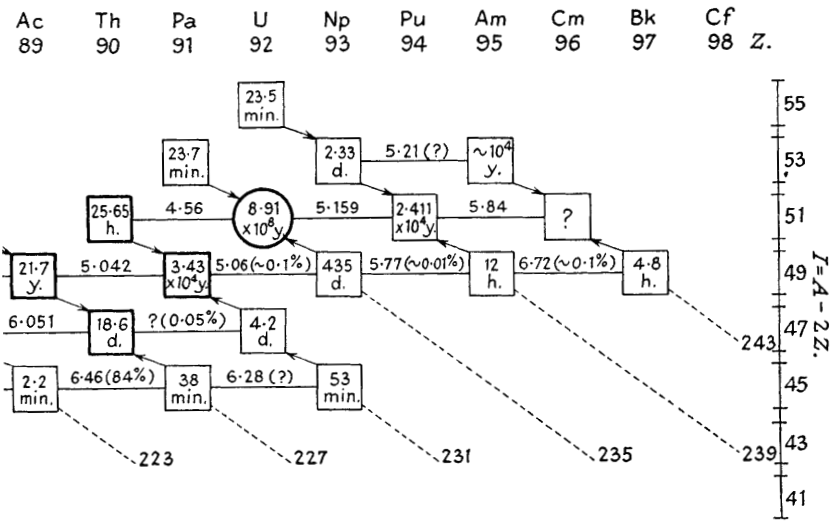


FIG. 4.—$4n + 3$ SERIES.

following year several investigations of the deuteron bombardment of heavy elements were reported. The bombardment of mercury [128] yielded ^{196}Tl and ^{197}Tl, although the correct isotopic assignments of these activities were not immediately apparent (d,2n reactions). The 11·5-day ^{202}Tl was obtained in the same bombardments and this assignment was confirmed by the production of the same activity by the fast-neutron irradiation of thallium. The 68-minute nuclear isomer of ^{204}Pb and the 52-hour ^{203}Pb were produced by the bombardment of thallium and the assignment of the latter was confirmed by its production from lead by the (n,2n) reaction. The bombardment of lead [129] gave ^{206}Bi by the (d,2n) reaction and polonium was obtained by an analogous reaction with bismuth.[130]

Astatine.—To the radiochemist perhaps the most interesting development following the operation of the 60″ Berkeley cyclotron was the production of the first known isotope of element 85 – astatine ; ^{211}At was produced [131] by the bombardment of bismuth with 25 M.e.v. helium ions. Fortunately, the isotope proved to be of sufficiently long half-life to permit the study of its chemistry by tracer methods.[132] It is, indeed, still the longest-lived isotope of this element known. The decay characteristics of the isotope proved unusual ; the overall half-life was found to be 7·5 hours, but it was shown that decay takes place both by α-emission and by orbital-electron capture. The branching ratio α/K was shown to be 2/3. Identification of one of the daughter nuclei as Ac-C' established the isotopic assignment ; the other daughter has not yet been detected. The isotope was the first discovered of the now numerous group of heavy nuclei found to decay partly or entirely by orbital-electron capture (see p. 298).

Although the half-life is too short for convenient operation on a microchemical scale, some details of the chemical behaviour of the element have been obtained by tracer studies. Astatine can be separated from the bismuth target by volatilisation. The element is readily volatilised from a glass substrate even at room temperature ; but on silver it is fixed even at 300° c., presumably owing to the formation of silver astatide. The element dissolves in water and can be extracted from aqueous solutions in the acid or nearly neutral pH ranges by such solvents as benzene or carbon tetrachloride. It cannot be solvent extracted from alkaline solutions in which it may hydrolyse to the AtO^- and At^- ions. Astatine is reduced to an anionic state, probably the At^- ion, by sulphurous acid or by zinc. In this form it co-deposits on silver or thallous iodide in acid or alkaline solution. Bromine and ferric salts oxidise astatine to another anionic state, which does not co-deposit on silver iodate, and which may be the same state as is formed by the alkaline hydrolysis of the element. More vigorous oxidising agents such as hypochlorous acid or argentic ions give a different anion, probably the astatate or AtO_3^- ion. In this form astatine

[128] Krishnan and Nahum, *Proc. Camb. Phil. Soc.*, 1940, **36**, 490.
[129] Fajans and Voigt, *Physical Rev.*, 1941, **60**, 619.
[130] Cork, Halpern, and Tatel, *ibid.*, 1940, **57**, 371.
[131] Corson, Mackenzie, and Segré, *ibid.*, p. 459.
[132] Johnson, Leininger, and Segré, *J. Chem. Physics*, 1949, **17**, 1.

co-deposits on silver iodate. Surprisingly, it has been reported that astatine concentrates with iodine in the thyroid gland.[133]

Fission and the Transuranic Elements.—The realisation of the nature of the action of thermal neutrons on uranium by Hahn and Strassmann [134] at the beginning of 1939 swept away the intricate radiochemistry of the supposed transuranic elements that they had developed during the five years since the first report of this complex reaction. For nearly a year it seemed possible that transuranic elements could not be obtained from this reaction, but the discovery [17] of the β-active ^{239}U, formed by radiative capture in the ^{238}U isotope, required the existence of at least one such element. The decay product was soon isolated and shown to be yet another short-lived β-active body.[135] It was used to study the chemical behaviour of the new element, neptunium. The β-activity of the isotope implied the existence of yet another transuranic element but no activity attributable to this daughter product could be detected, suggesting that it might eventually prove to be a long-lived α-active body. Similar difficulties [136] attended the detection of the daughter of the β-active ^{237}U which was discovered in the same year.

Subsequent international developments and the creation of the United States Manhattan Project delayed publication of the discoveries of the next few years until some two or three years after the end of the war. The majority of these investigations were conducted by Seaborg and his collaborators at Berkeley, California. A complete account of the achievements of this period has appeared in Volume 14B, Division IV, National Nuclear Energy Series (McGraw-Hill, N.Y., 1949).

The chemical properties of the transuranic elements have already been discussed in these Reviews.[137] This account will therefore be confined to some considerations of the nuclear properties of the isotopes of these elements.

Late in 1940 the deuteron bombardment of natural uranium, by means of the very energetic deuterons accelerated in the 60″ Berkeley cyclotron, led to the isolation of the first isotope of element 94 – plutonium.[138] The bombardment produced another short-lived isotope of neptunium, ^{238}Np, by the $(d,2n)$ reaction on ^{238}U. It was accompanied by ^{239}U and ^{239}Np, the former being produced by the (d,p) reaction on ^{238}U. The new isotope of neptunium decayed by β-emission with the formation of a shorter-lived α-active isotope of plutonium, ^{238}Pu. By the use of this isotope, analytical procedures for the separation of plutonium were developed [139] and, later in the same year, these were applied to the isolation [140] of the long-lived

[133] Hamilton and Soley, *Proc. Nat. Acad. Sci.*, 1940, **26**, 483.
[134] *Naturwiss.*, 1939, **27**, 11.
[135] McMillan and Abelson, *Physical Rev.*, 1940, **57**, 1185 ; Segré, *ibid.*, 1939, **55**, 1104.
[136] McMillan, *ibid.*, 1940, **58**, 178.
[137] Lister, *Quart. Reviews*, 1950, IV, No. 1, 20.
[138] Seaborg, Wahl, and Kennedy, National Nuclear Energy Series, Div. IV, Vol. 14B (McGraw-Hill, 1949, N.Y.), Paper 1.1a.
[139] Seaborg and Wahl, *ibid.*, Paper 1.6.
[140] Kennedy, Seaborg, Segré, and Wahl, *ibid.*, Paper 1.2.

α-active ^{239}Pu, formed by the β-decay of ^{239}Np. In a similar manner separation procedures developed by using ^{239}Np were applied in 1942 [141] to the isolation of the long-lived α-active daughter of the β-active ^{237}U. About the same time a thorium target was bombarded and a short-lived β-active protactinium isotope, ^{232}Pa, formed by the $(d,2n)$ reaction, was obtained. Its decay product was identified as a relatively short-lived α-active uranium isotope.[142]

The heavy demands made on the staff by the *ad hoc* technical developments of the project rendered the next two years unfruitful, but by mid-1944 opportunities arose for the study of further heavy-element reactions by use of very energetic deuterons and helium nuclei. Meanwhile three important new resources had become available to the investigators from different parts of the Manhattan project. Macroscopic quantities of plutonium (^{239}Pu) had been extracted [143] and sufficient was available for the preparation of cyclotron targets. Another branch, responsible for the separation of the natural uranium isotopes, was able to provide macroscopic quantities of nearly isotopically pure ^{238}U and ^{235}U. Somewhat later macroscopic [144] quantities of the long-lived ^{237}Np also became available. In addition, the completion of a number of reacting piles provided facilities for irradiation with very much greater thermal-neutron fluxes than had ever been possible before. The cyclotron could produce a thermal neutron flux of 10^8 neutrons/cm.^{2}/sec., but the piles could provide a flux 10^4 as great over a much larger working volume.

The third transuranic element to be discovered,[145] element 96 – curium, was identified at the end of the summer of 1944 as a product of the bombardment of plutonium with 40 M.e.v. helium ions. The α-active isotope ^{242}Cm, formed by the (α,n) reaction, was the first to be characterised; but early the following year ^{240}Cm, formed simultaneously by the $(\alpha,3n)$reaction, was identified. Isotopic allocation of both activities was achieved by identification of the ^{238}Pu and ^{236}Pu produced by their decay. Subsequent investigations [146] revealed that ^{238}Cm and ^{241}Cm, formed by the $(\alpha,5n)$ and the $(\alpha,2n)$ reaction respectively, could also be isolated from the products of this bombardment.[147]

The last of these curium isotopes was a member of the now numerous group of nuclei in this mass region that decay partly or entirely by orbital-electron capture. None of these mass-deficient heavy nuclei, so far reported, exhibits positron emission. The heaviest nucleus [148] of this kind is ^{192}Au, although the energy of the γ-rays accompanying the decay of several of these orbital-electron capturing nuclei, including, for example, ^{203}Pb, ^{205}Bi,

[141] Wahl and Seaborg, National Nuclear Energy Series, Div. IV, Vol. 14B (McGraw-Hill, 1949, N.Y.), Paper 1.5.
[142] Gofman and Seaborg, *ibid.*, Paper 19.14.
[143] Cunningham and Werner, *ibid.*, Paper 1.8.
[144] Magnusson and La Chapelle, *ibid.*, Paper 1.7.
[145] Seaborg, James, and Ghiorso, *ibid.*, Paper 22.2.
[146] James, U.S. Atomic Energy Commission, A.E.C.D. 2224. Declassified Aug. 1948.
[147] Seaborg and Perlman, *Rev. Mod. Physics*, 1948, **20**, 585.
[148] Wilkinson, *Physical Rev.*, 1949, **75**, 1019.

^{206}Bi, ^{234}Np, and ^{240}Am,[128, 149] show that the disintegration energy is more than sufficient for positron production (*i.e.*, the γ-ray energy exceeds 1·1 M.e.v.). Although the probability of finding K electrons within the nucleus will be greater for the heavier nuclei, positron emission may still be expected to be the dominant process when energetically possible. The apparently numerous exceptions must result from the wider choice of energy levels open to the product of orbital-electron capture, because this process does not expend energy by the production of the rest mass of two electrons as occurs with positron emission. Thus, although the selection rules governing both modes of decay are the same, the choice of transitions possible for orbital-electron capture may include much less strongly forbidden transitions than are involved for positron emission.

Towards the end of the same year the fourth transuranic element, americium, of atomic number 95, was discovered.[150] The products of the bombardment of ^{238}U and ^{235}U targets with 40 M.e.v. helium ions were investigated and amongst the numerous isotopes of plutonium which were detected was a rather long-lived β-active species ^{241}Pu [^{238}U(α,n), ^{241}Pu]. The daughter of this isotope proved to be a long-lived α-active isotope of element 95 – ^{241}Am. The other products of the bombardment included isotopes of plutonium of mass numbers from 236 to 241, inclusive. The half-life and radiation characteristics of each were determined. Later,[66] several other isotopes of americium were prepared by the deuteron bombardment of plutonium. These included ^{238}Am, ^{239}Am, and ^{240}Am, all of which decay by orbital-electron capture, accompanied in the case of the last two isotopes by α-particle emission.

Important alternative modes of production of some of these nuclei, by neutron irradiation, were discovered during later investigations. Other experiments had shown that, although the fission cross-section of ^{239}Pu for thermal neutrons was very large, yet the cross-section for the alternative process of de-excitation of the compound nucleus by photon emission, *i.e.*, radiative capture, was of comparable order of magnitude. As a result, prolonged neutron irradiation of plutonium was found [151] to produce the long-lived α-active isotope, ^{240}Pu, which had previously been identified amongst the products of the helium-ion bombardment of uranium ; but the ^{240}Pu itself possessed a considerable thermal-neutron capture cross-section giving rise to ^{241}Pu, the β-active parent of ^{241}Am. The detection of such products of multiple thermal-neutron capture was only feasible by using the very high neutron fluxes available in the piles. By these reactions americium is continually produced in the uranium slugs in a pile. The considerable fast-neutron flux in the uranium in the piles gives ^{237}U by the (n,2n) reaction. This soon decays to ^{237}Np, so that the plutonium in the slugs is accompanied by macroscopic amounts of both neptunium and

[149] Karraker and Templeton, see Nat. Bur. Stand. Circ. 499 ; Hyde, Studier, and Ghiorso, National Nuclear Energy Series, Div. IV, Vol. 14B (McGraw-Hill, 1949, N.Y.), Paper 22.15.

[150] Street, Ghiorso, and Seaborg, *Physical Rev.*, 1950, **79**, 530.

[151] Ghiorso, James, Morgan, and Seaborg, *ibid.*, 1950, **78**, 472.

americium. The neptunium content of the slugs may amount to 0·1% of the plutonium.[152]

Neutron irradiation of separated samples of ^{241}Am was found to give rise to a pair of isomeric nuclei.[153] One isomer was β-active with a half-life of 16 hours. Its decay product was identified as the previously-mentioned ^{242}Cm. The lower-lying isomer showed α/β branching with a half-life of about 400 years. Prolonged neutron irradiation [150] was found to produce a very long-lived α-active isotope, ^{243}Am, together with a short-lived β-active isotope, ^{244}Am, which yields an α-active daughter of some 20 years' half-life, the longest-lived curium yet described.

Quite recently, with the separation of macroscopic samples of ^{241}Am and ^{242}Cm, the products of the helium-ion bombardment of these nuclei have been examined and isotopes of elements 97 and 98 have been characterised. These elements have been called berkelium and californium, respectively. The α-active ^{244}Cf of half-life 45 minutes was obtained from curium [154] by the $(\alpha,2n)$ process, and ^{243}Bk, decaying by α-emission and orbital-electron capture with a half-life of 4·6 hours, was obtained in a similar manner from americium.[155] Only the α-energy of the curium daughter of the latter isotope has so far been reported.[156]

The latest discovery in this field promises considerable development in the future. By accelerating stripped carbon ions (C^{6+}) in the cyclotron,[157] the following reactions [158] have already been effected—$^{238}U(C^{6+},6n)^{244}Cf$; $^{238}U(C^{6+},p6n)^{243}Bk$. The problem of adjusting the cyclotron to the acceleration of these carbon ions is simplified by their possessing nearly the same charge-to-mass ratio as the deuteron or α-particle; but the energy attained under similar accelerating conditions will be about 6 times as great for the carbon ions as for the deuterons. It will be observed that similar bombardments of neptunium and plutonium should lead to the isolation of elements 99 and 100.

Some chemical properties of berkelium and californium have been briefly reported. Their behaviour on an ion-exchange column suggests a stable tervalent aqueous ion. Evidence for a higher valency state of berkelium has been obtained.

Technical Aspects of Transuranic-element Production.—It has already been observed that the preparation of isotopes of the transuranic elements was intimately associated, first with the construction of ion-accelerating devices capable of producing sufficiently energetic bombarding particles to penetrate the Coulomb barrier of the highly charged heavy nuclei; and later with the development of nuclear reactors, possessing enormous potentialities for intense neutron irradiation. Both these instruments have been

[152] Seaborg, National Nuclear Energy Series, Div. IV, Vol. 14B (McGraw-Hill, 1949, N.Y.), Paper 22.3. [153] Manning and Asprey, *ibid.*, Paper 22.7.

[154] Thompson, Street, Ghiorso, and Seaborg, *Physical Rev.*, 1950, **78**, 298.

[155] Thompson, Ghiorso, and Seaborg, *ibid.*, 1950, **77**, 838.

[156] *Idem*, U.S. Atomic Energy Commission, A.E.C.D. 2880, Declassified July 1950.

[157] Miller, Hamilton, Putnam, Raymond, and Rossi, U.S. Atomic Energy Commission, U.C.R.L. 881, Aug. 1950; *Physical Rev.*, 1950, **80**, 486.

[158] Ghiorso, Thompson, Street, and Seaborg, *ibid.*, 1951, **81**, 154.

developed substantially since 1945. The ordinary cyclotron is unable to accelerate particles above a certain energy because the relativistic increase in the mass of the fast-moving ion requires a stronger magnetic field near the perimeter of the cyclotron magnet. To some extent this can be provided by shimming the magnet faces, but eventually this expedient leads to defocusing of the ion beam so that the ion current decreases rapidly as the energy of the accelerated particles increases. It has been shown [159] that this limitation to the maximum energy can be avoided if the oscillator frequency of the power supply to the cyclotron **D**'s is modulated to accommodate the variation in mass.[160]

The frequency-modulated cyclotron or synchrocyclotron can accelerate ions to much greater energies ; for instance, the new 184″ Berkeley synchrocyclotron can produce 400 M.e.v. helium ions. The first experiments on the operation of a frequency-modulated cyclotron were conducted with the old 37″ Berkeley instrument.[161] At such high energies an important difference in the nature of the nuclear transformations begins to take effect.[162] The reaction no longer proceeds by formation of a compound nucleus, whose disintegration is more or less independent of its mode of formation, but the very energetic bombarding particle sweeps out one or more nuclear particles without immediate effect on the rest of the nucleus. Very destructive reactions, called spallation,[163] can be caused, and many of the heavy elements, not exhibiting ordinary fission, suffer this reaction with such energetic bombarding particles. Reactions such as $(\alpha,4n)$; $(\alpha,5n)$; $(\alpha,p6n)$ are commonly observed.

Until the conclusion of the late war the cyclotron was almost the only accelerating device used by the radiochemist in the study of the heavy elements, but since then several other machines have achieved potential or actual importance. Two methods of accelerating electrons to energies in excess of 100 M.e.v. have been discovered and both have proved satisfactory in action. In the Betatron, devised by Kerst [164] in 1940, the electrons are accelerated in a circular orbit of constant radius by the use of a varying magnetic field. The pole pieces of the magnet are cut away round the orbit and to the circumference of the magnet, so that the field at the orbit of the electrons increases at half the rate at which the average flux within the orbit increases. Focusing is achieved by a radial variation of the field in the region of the orbit such that the electrons describe damped oscillations about their mean path.

The principle of the synchrotron was established independently by McMillan and Veksler.[159] The electrons are again confined to a circular orbit by a varying magnetic field proportional to the momentum of the

[159] McMillan, *Physical Rev.*, 1945, **68**, 143 ; Veksler, *J. Physics U.S.S.R.*, 1945, **9**, 153.

[160] Bohm and Foloy, *Physical Rev.*, 1947, **72**, 649.

[161] Richardson, Mackenzie, Lofaren, and Wright, *ibid.*, 1946, **69**, 669.

[162] Serber, *ibid.*, 1947, **72**, 1114.

[163] Perlman, Goeckermann, Templeton, and Howland, *ibid.*, p. 352 ; Goeckermann and Perlman, *ibid.*, 1949, **76**, 628.

[164] *Ibid.*, 1946, **58**, 841.

electrons, but the energy increment is supplied, as in a cyclotron, by a radio-frequency oscillator feeding a pair of **D**'s. In this instrument a central magnetic field is unnecessary and a much cheaper annular magnet may be employed. The instrument differs from the cyclotron in using a varying magnetic field to confine the moving particles to a circular, as opposed to a spiral, orbit.

These very energetic electrons have been used to excite very hard γ-radiation, with which it is possible to induce photo-disintegration of even the heavy nuclei; for example, ^{203}Pb has been obtained from lead by the (γ,n) reaction.[165]

It is possible, in principle, to accelerate heavy positive ions by this method providing the ions can be injected into the synchrotron at an energy at which they travel at substantially the same velocity as light. For electrons this is already true at 2 M.e.v. but for protons it is not even true at 200 M.e.v. However, by wide-band frequency modulation of the radio-frequency accelerating potential, it is possible to confine even a heavy ion to an orbit of constant radius. Proton synchrotrons based on this possibility are at present under construction.[166] Several other machines, using a variety of accelerating principles and designed to produce positive ions of between 100 and 1000 M.e.v., are now being made in various parts of the world.[167]

The extension of pile facilities has been no less considerable.[168] The thermal-neutron fluxes available have increased by three orders of magnitude. Thus the Harwell G.L.E.E.P., the earlier low-energy pile,[169] provided a flux of 3×10^{10} neutrons/cm.^{2}/sec.; the B.E.P.O., a rather more powerful air-cooled pile,[170] provides a flux of 2×10^{12} neutrons/cm.^{2}/sec., and the Canadian N.R.X. heavy-water[171] pile gives 2×10^{13} neutrons/cm.^{2}/sec. Besides these, fast-neutron reactors[172] have been constructed which will provide large fast-neutron fluxes and, taken in conjunction with the predominantly thermal neutron flux in the graphite "thermal column", which is attached to most experimental piles, very large fluxes of almost any desired neutron spectrum can now be obtained.

The separation and identification of the products obtained from these machines was only possible as a result of far-reaching improvements in radiochemical manipulation. Many of the reactions studied were accompanied by fission reactions so that it was found necessary to handle rela-

[165] Hanson, Duffield, Knight, Diven, and Palevsky, *Physical Rev.*, 1949, **76**, 578.

[166] Farly, U.S. Atomic Energy Commission, A.E.C.U. 326; Livingston, Haworth, Blewett, and Green, *ibid.*, A.E.C.U. 337; Lofgren, *ibid.*, U.C.R.L. 493, Oct. 1949; U.C.R.L. 557, Dec. 1949; Hibbard, *Nucleonics*, 1950, **7**, No. 4, 30; Brobeck, *Rev. Sci. Instr.*, 1948, **19**, 545.

[167] Woodyard, *Elec. Eng.*, 1948, **67**, 759; Thomas, Mittelman, and Goldsmith, Brookhaven Nat. Lab. Report (U.S.), BNL. L. 101, July 1948; McMillan *Helv. Physica Acta*, 1950, **23**, Suppt. 3, 11.

[168] U.S. Atomic Energy Commission, A.E.C.U. 291.

[169] Colmer and Littler, *Nucleonics*, 1951, **8**, No. 1, 3.

[170] "Radioactive Materials and Stable Isotopes", Catalogue No. 2, A.E.R.E.

[171] Keys, *Atomics*, 1950, **1**, 262.

[172] Hall and Hall, U.S. Atomic Energy Commission, M.D.D.C. 1080.

tively large activities. The products themselves were often highly α-active substances of very great toxicity if inhaled as a dust. For these reasons considerable attention was paid to the methods of handling the products.[173] The nascent targets or irradiated substances often had to be processed by partial or complete remote control. α-Active products were generally handled in a controlled atmosphere by means of " dry boxes ", thus avoiding exposure of the operator to even the minutest trace of active substance.[174]

None the less important was the high degree of efficiency of separation required of the chemical procedures in order to reduce the contamination of a desired product by subsidiary activities, often present in much greater amounts. The complexity of this problem is illustrated by a report on the decontamination of ^{239}Np by Fields.[175] In several cases one or more contaminating activities had to be reduced to less than 10^{-7} of the initial concentration by repeated chemical separation. A collection of several of these procedures has recently been published.[176]

A more spectacular development took place in the microchemical investigation of these elements. In every case the amount of the element initially available was not more than a few micrograms ; but by means of ultramicrochemical techniques developed by Kirk and his collaborators very extensive surveys of the chemical behaviour of these elements were accomplished. By these means reliable separation procedures were established and each successive long-lived isotope was separated for use as a target material for further transformations. A detailed review of these techniques has been made by Cunningham.[177]

A New Radioactive Series

The $4n + 1$ Series (Neptunium Family).—A few years after the principal features of the three natural radioactive decay series had been established, Russell [9] observed that a fourth series, composed of isotopes of the heavier elements whose mass numbers could be expressed in the form $4n + 1$ (n integral), might be expected. But no evidence of the existence of naturally occurring members of this series was forthcoming although pleochroic haloes were discovered that could not be attributed to any of the then known α-active substances.[178]

The classification of nuclei by their mass numbers into four series is not as arbitrary as at first might appear, since a member of one series cannot change to another by a radioactive transformation (the very rarely observed phenomenon of neutron emission being excluded). The nuclear forces begin to show saturation when the nucleus contains more than four particles, and

[173] Tompkins, U.S. Atomic Energy Commission, M.D.D.C. 1414.

[174] Sheinberg and Thomas, *ibid.*, A.E.C.D. 1866.

[175] National Nuclear Energy Series, Div. IV, Vol. 14B (McGraw-Hill, 1949, N.Y.), Paper 15.10.

[176] Meinke, U.S. Atomic Energy Commission, A.E.C.D. 2738, Declassified Oct. 1949 ; A.E.C.D. 2750, Declassified Dec. 1949.

[177] *Nucleonics*, 1949, **5**, No. 5, 62.

[178] Schintlmeister, *Ber. Akad. Wiss. Wien*, 1935, Abt. 2*a*, **144**, 475.

several properties show regularities if the nuclei are grouped in these four series.

Predictions [179] of the form the missing decay series might take were made by Russell, but until the discovery of artificial radioactivity the heaviest nucleus in this series was the stable ^{209}Bi. The synthesis of ^{209}Pb, ^{233}Th, ^{233}Pa, and ^{237}U has already been described, and with the benefit of this additional information further predictions were made by Turner [78] and Ponisovsky.[180] The scheme proposed by the former author was supported by Feather and has now been substantiated by experimental evidence (see Fig. 2).

Early in 1942 the long-lived α-active uranium, formed by the β-decay of ^{233}Pa, was detected,[141] and after the separation of a 4-microgram sample it was shown to undergo fission by thermal neutrons with a cross-section comparable with that of ^{235}U. Upon this discovery the isotope began to assume importance in the Manhattan project. The following year, ^{237}Np was isolated, and since this remains the longest-lived member of this series it has been suggested that the series should be known as the neptunium series.[153] The quantities of both ^{237}Np and ^{233}U that were available at this time were quite inadequate to enable the details of their decay products to be disentangled, particularly since the thorium daughter of ^{233}U was later found to be relatively long-lived ; but in 1944 it was decided to prepare milligram quantities of the ^{233}U for nuclear physical studies. To this end some thorium was subjected to a long irradiation with neutrons in the pile and by the Autumn some 10 milligrams of the isotope were isolated. Using this material parallel, but independent, studies of the decay products were carried out by American and Anglo-Canadian research teams.[181]

The product was purified by solvent extraction as uranyl nitrate, by precipitation as peruranic acid, and finally by a second solvent extraction. A mass-spectrometric examination showed it to contain between 4 and 5% of ^{238}U, whose origin was assumed to be the natural uranium impurity of the thorium compound irradiated ; but because of the long half-life of ^{234}U the product was not appreciably contaminated with the decay products of the uranium series. However, a more serious impurity was not revealed by this analysis, but appeared on examination of α-ray spectrum of the thorium daughter of the ^{233}U. The spectrum of the freshly separated ^{229}Th showed, in addition to a strong and previously unknown α-energy attributed to the ^{229}Th, a more energetic group, representing about 30% of the total α-activity, that was identified with radiothorium. Subsequent investigation confirmed that the ^{233}U was contaminated with ^{232}U, which forms Rd-Th by α-emission.[142] Although only about 1 α-particle in 6000 emitted from the purified ^{233}U sample was due to ^{232}U, the half-life of Rd-Th (^{228}Th) is so much less than that of ^{229}Th that the radioactive con-

[179] Widdowson and Russell, *Phil. Mag.*, 1924, **48**, 293.

[180] *Nature*, 1943, **152**, 187.

[181] Hagemann, Katzin, Studier, Seaborg, and Ghiorso, *Physical Rev.*, 1950, **79**, 435 ; English, Cranshaw, Demers, Harvey, Hincks, Jelley, and May, *ibid.*, 1947, **72**, 253 ; Hagemann, Katzin, Studier, Ghiorso, and Seaborg, *ibid.*, p. 252.

tamination of the latter isotope is very noticeable. In the same way the freshly separated radium daughter of the ^{229}Th is considerably contaminated by Th-*X*. The origin of the ^{232}U contamination is uncertain, but ^{231}Pa is known to possess a very large neutron-capture cross-section, the product ^{232}Pa is a short-lived β-active body, parent of ^{232}U. The protactinium might be present as a natural impurity in the thorium or might also be produced from the thorium by the $(n,2n)$ reaction and subsequent β-decay of the U-*Y*.

^{229}Th, daughter of the ^{233}U, was found to be separated conveniently by adjusting the pH of the solution to about 4, under which condition thorium salts are extensively hydrolysed, and then centrifuging the solution at very high speed. The thorium adhered to the walls of the centrifuge tube and was thoroughly washed before solution in nitric acid. After the Rd-Th daughters had grown to equilibrium, the α-activity of the sample continued to grow with an apparent half-life of about three weeks. Thereafter it remained constant, showing that ^{229}Th must be relatively long-lived. Equilibrium solutions of this thorium isotope proved convenient for the study of the other decay products.

The number and energy of the α-particles emitted during the decay processes, which must lead to the stable ^{209}Bi, were investigated by two methods. In the first, specially prepared photographic plates were impregnated with very small activities of ^{233}U and ^{229}Th. After storage for varying periods of time the plates were developed and examined under a high-power microscope. The α-particles produce tracks of developed nuclei in the plates, the length of the track depending upon the energy of the α-particle. If an atom suffers successive α-disintegrations, stars formed by an equivalent number of tracks emanating from a common origin are seen in the plate. The ^{233}U plates showed a preponderance of single tracks with an occasional two- or six-track star. The ^{229}Th plates contained only five-track stars, and occasional single tracks. These results showed that the ^{229}Th possessed a long half-life but the daughter activities were all short. By calibration of the plates with α-particles of known energies, the α-ray energies of the ^{233}U decay products were calculated.

Alternatively, the α-particles can be examined by means of an ionisation chamber and pulse analyser. The α-active sample is placed in a specially designed [182] fast ionisation chamber in which the whole of the ionisation released by the dissipation of the particle energy within the gaseous dielectric is collected and the pulse so obtained is amplified in a linear amplifier. The chamber is usually provided with a grid to avoid positive-ion effects. The output pulse from the amplifier, which is proportional to the energy of the initiating particle, is fed to the pulse analyser which sorts according to size and records each in an appropriate channel. A rapid and quantitative record of the α-particle spectrum of the source material is obtained. An examination of the ^{233}U made in this way revealed five new α-energies besides those due to the ^{233}U itself and to ^{232}U and its decay products.

[182] Cranshaw and Harvey, *Canadian J. Res.*, 1948, **26**, *A*, 243 ; Bunemann, Cranshaw, and Harvey, *ibid.*, 1949, **27**, *A*, 191.

The attack on the problem was begun from both ends of the chain, and, because of the ease that distinguishes separations made by means of the isotopes of radon, an early search for a radon isotope was made. However, experiments conducted *in vacuo* under conditions favourable to the detection of a short-lived radon isotope failed to detect such an activity although the thoron from Rd-Th could be observed. Since the photographic-plate experiments and the growth of α-activity in the ^{229}Th samples precluded the existence of a longer-lived radon isotope, it was concluded either that the decay products did not include an isotope of radon or that it must be very short-lived indeed.

Electrolytic separations yielded immediate results. Traces of lanthanum, barium, bismuth, cæsium, and lead carriers were added to an equilibrium solution of the ^{229}Th in 1N-nitric acid. After an hour of electrolysis with platinum electrodes the cathode was found to be both α- and β-active. Both activities decayed initially with a half-life of about 50 minutes. Examination by the photographic-plate method gave single tracks whose length corresponded to that of the most energetic α-particle group found with the ^{229}Th. By means of a coincidence arrangement it was shown that the α- and β-particles are emitted almost simultaneously. The use of a delay circuit proved that the α-particle followed the β-ray and the half-life of the former activity was about 10^{-5} second.[183] The attribution of the β-activity to a bismuth isotope was confirmed by precipitation of the bismuth from 3N-nitric acid as phosphate, dissolution of the phosphate in hydrochloric acid, and reprecipitation of the bismuth as sulphide. The α- and β-activity followed the bismuth quantitatively throughout this separation. Rotation of a silver foil in a weakly acidic solution of the ^{229}Th source, or precipitation of tellurium by stannous chloride in the same solution, failed to remove either activity. This behaviour is to be expected from a 50-minute β-active bismuth isotope with a very short-lived α-active polonium daughter. Later and more precise measurements showed that the half-life of the bismuth isotope was 47 minutes, and the maximum β-ray energy determined by absorption measurements 1·2 M.e.v.

The radium isotopes were separated from the ^{229}Th source solution containing carriers by co-precipitation on barium nitrate from very concentrated nitric acid solution. The precipitate was dissolved in the minimum amount of water, and barium chloride precipitated by hydrogen chloride gas. The interpretation of the decay curve found for the radium was confused by the thorium-*X* contamination. Preliminary experiments showed a steadily decreasing α-activity, suggesting that the radium isotope was itself α-active. Indeed, freshly extracted samples showed very slight β-activity with the usual Geiger-Mueller counters; but the apparent absence of a radon isotope and the discovery of the contamination by Rd-Th decay products led to a reconsideration of this result.

The complications arising from the Th-*X* were avoided by separating a radium sample, allowing the Th-*X* to decay, and repeating the purification of the radium from its own decay products, including a separation of the

[183] Jelley, *Canadian J. Res.*, 1948, **26**, *A*, 255.

actinium isotopes on a lanthanum fluoride precipitate. The α-activity of the purified radium sample was found to grow to a maximum after about 20 days and then to decay. An analysis of the growth and decay curve suggested that the ^{225}Ra might be β-active with a half-life of about 15 days, giving rise to an α-active actinium daughter of half-life about 10 days, all the subsequent decay products being short-lived. Confirmation of this hypothesis was obtained by the detection of the very soft β-particles emitted by the freshly purified ^{225}Ra source.

It was apparent that the ^{233}U was parent of a long-lived α-active ^{229}Th, which in turn was parent of a β-active radium isotope ^{225}Ra of half-life about 15 days and which produced an α-active actinium, ^{225}Ac, of comparable half-life. In addition, it seemed likely that the chain proceeded through α-active francium and astatine isotopes, as had already been predicted. The disintegration of the astatine presumably gave rise to the bismuth activity previously described, which must therefore be ^{213}Bi, so that the chain would reach ^{209}Bi *via* the already known ^{209}Pb.

Later, samples of ^{225}Ac were separated, and the half-life determined to be 10 days. The α-energy was identified in the pulse analyser and by photographic plates. The plates showed nearly all the α-tracks emanating from four-pointed stars. A careful analysis of the growth and decay of α-activity in a separated sample of ^{225}Ra showed the half-life to be 14·8 days. The maximum β-ray energy for the isotope was shown to be about 160 K.e.v. by absorption measurements.

The anodic deposits obtained by electrolysis of a 2N-nitric acid solution of the ^{229}Th equilibrium source were then examined. The lead peroxide was found to be β-active, decaying with a half-life of 3·3 hours. The radiation characteristics were identified with those previously reported for ^{209}Pb. The allocation of the bismuth and polonium activities to ^{213}Bi and ^{213}Po was therefore confirmed.

A rapid examination of the α-ray spectrum of a freshly separated sample of ^{225}Ac by means of the pulse analyser revealed that both the remaining unidentified α-activities grew in the sample with a half-life of about 5 minutes. The most energetic α-group, due to ^{213}Po, grew with a half-life of about 50 minutes, confirming the attribution of this activity. Because the 5-minute period could be observed, it followed that both these activities must precede the ^{213}Bi. It seemed reasonable to suppose that ^{221}Fr was α-active with a half-life of about 5 minutes and that its daughter ^{217}At was very short-lived. These suppositions were proved by separation of the francium on a cæsium perchlorate precipitate. The α-active ^{221}Fr decayed with a half-life of 4·8 minutes. The pulse analyser showed that only the two previously unassigned α-energies were present. Display of the α-particle pulses on an oscilloscope led to the discovery that they were generally emitted in pairs. By arranging for a carefully calibrated time base of the cathode-ray tube to be triggered by the primary α-particle and for the tube to be photographed at each sweep, the distribution of time intervals between the pairs of α-particles was measured. In this way the half-life of the ^{217}At was shown to be 0·02 second. The ^{221}Fr could also

be separated from a ^{225}Ra–^{225}Ac source on a barium chloride carrier by volatilisation together with the ^{213}Bi. The growth of α-activity in the residual source indicated periods of 5 and 47 minutes.

Finally, an attempt was made to measure the half-life of the long-lived ^{229}Th. A weighed quantity of ^{233}U was separated from its decay products by solvent extraction, and after this had stood for a measured period a known quantity of U-X_1 was added. Zirconium was added as carrier, and the thorium isotopes precipitated on zirconium iodate in 2N-nitric acid. The iodate was dissolved in sulphurous acid, and the precipitation repeated. The thorium isotopes were then separated on a small lanthanum fluoride precipitate. The recovery of the U-X_1 determined the efficiency of the chemical separation. The α-activity due to the ^{229}Th was measured by means of the pulse analyser, which allowed the contribution to the activity from the Rd-Th contamination to be ignored. After correction for the separation efficiency, the rate of growth and half-life of the ^{229}Th could be calculated.

Since α/β branching of the ^{213}Bi had been predicted, a more detailed study of this isotope was made by means of the pulse analyser. A weak additional α-particle group of much lower energy than that due to ^{213}Po was detected. It exhibited the same half-life as the ^{213}Bi and represents an alternative mode of decay. Much more recently the β-active ^{209}Tl formed by this branch has been isolated and shown to have a half-life of 2·2 minutes and to emit β-particles of maximum energy 1·8 M.e.v.[184]

Several transuranic isotopes belonging to this series (^{237}Np, ^{237}Pa, ^{241}Pu, ^{241}Am, and ^{241}Cm) have been discussed earlier in this Review.

Before the discovery of this series several hypotheses were advanced to explain its absence from natural sources.[185] The ultimate reason is now known to lie in the short half-lives of all its members. These preclude detection in rocks unless some member of the series is continually generated by nuclear transformation. It is true that the neutrons released by the spontaneous fission of uranium must occasionally lead to the formation of ^{237}U by the $(n,2n)$ process in uranium minerals. The ^{237}U will decay to produce ^{237}Np and other members of the series but the activities produced in this way are so small that they escape detection, even by means of the very sensitive photographic-plate technique. It is possible [186] that evidence of the previous existence of the neptunium family remains in some rocks and the unidentified pleochroic haloes have been reinvestigated, the α-energies reported for the members of the series being borne in mind. The results are incompatible with the identification of the nuclei of these haloes with any member of the series.

Although the immediate reason for the absence of the neptunium family is now apparent, it is more difficult to explain why these nuclei should be so unstable. It is generally true that the members of the odd series are less

[184] Hagemann, *Physical Rev.*, 1950, **79**, 534.

[185] Joliot-Curie, *Bull. Acad. Sci. U.R.S.S.*, Sér. Phys., 1936, **1-2**, 647.

[186] Poole, Delaney, and McCormick, *Sci. Proc. Roy. Dublin Soc.*, 1949, **25**, No. 9, 101; *Physical Rev.*, 1949, **76**, 1253.

stable than those of even series. Indeed, if the half-life of ^{235}U were but an order of magnitude less, the actinium series would not be found in natural sources and a much smaller reduction would render the construction of piles impossible. Our present knowledge of nuclear structure is insufficient to provide an answer to this question.

New Techniques in the Study of the Radioactive Series

One of the distinguishing features of the neptunium series is the absence of a radon isotope. The classical methods of investigation of the decay products in the natural series made considerable use of the sharp separation of the short-lived decay products possible by means of these isotopes. In these circumstances, it is doubtful if the decay mechanism of the new series could have been elucidated so quickly were it not for the development of two techniques capable of measuring and identifying the individual α-activities contained in a single sample of almost insignificant total activity.

The photographic-plate technique [187] is certainly not a recent discovery, the individual tracks produced by α-particles having been observed as long ago as 1911,[188] and the relation between the track length and particle energy determined the following year.[189] By impregnating plates with a known amount of active substance, exposing them for various measured periods, and determining the statistical distribution of stars with different numbers of tracks and the combinations of track lengths, the half-lives and α-particle energies of the parent substance and its decay products may be deduced. A combination of such observations with a few chemical separations will establish the identity and characteristics of the α-active decay products. These observations can all be conducted with a total activity of a few disintegrations per minute. Experiments of this kind were made on thorium [190] and its decay products in 1936. However, the thick photographic emulsions convenient [191] for these studies did not become generally available till 1946, although some special plates were produced commercially before the war. The technique requires some skill and the use of a powerful microscope equipped to measure track lengths, but is generally less expensive, though more time-consuming, than the pulse analyser and its associated apparatus.

The problem of designing an electronic instrument capable of classifying and recording pulses according to their height has long confronted the nuclear physicist.[192] A decade ago it was customary to obtain a permanent record of the pulses by photographing the movement of a fast string galvanometer, the mirror of a loop oscillograph, or the trace of a cathode-ray oscilloscope, and to determine the pulse size distribution by measurements

[187] Yagoda, "Radioactive Measurements with Nuclear Emulsions" (J. Wiley, 1949, N.Y.).

[188] Reinganum, *Physikal. Z.*, 1911, **12**, 1076.

[189] Michl, *Ber. Akad. Wiss. Wien*, 1912, Abt. 2*a*, **121**, 1431.

[190] Taylor and Dabholkar, *Proc. Physical Soc.*, 1936, **48**, 285; Guillot and Perey, *Compt. rend.*, 1947, **225**, 330.

[191] Demers, *Bull. Amer. Physical Soc.*, 1947, **22**, No. 3, 17.

[192] Lewis, Nat. Res. Coun. Report (Canada), DL-3, July 1949.

on the record. It is also possible to calculate the pulse size distribution curve from the bias curve obtained with an ordinary discriminator, which measures only the number of pulses exceeding some predetermined, but variable, value. To do this the bias curve must be differentiated. Thus every point on the derived curve embodies the errors in two determinations on the bias curve. Another disadvantage lies in the increased stability demanded of the amplifier to cover the considerable time required by the measurement of the bias curve.

The increasing urgency of the requirements of the Manhattan project and the allied British and Canadian groups stimulated a number of independent solutions, and several devices fulfilling these requirements by different mechanisms have now been constructed.

The earliest pulse analysers possessed but a single channel,[193] formed by two discriminating circuits whose bias voltages were separated by a predetermined voltage and arranged so that output pulses were obtained only when the incoming pulse passed the first discriminator but failed to pass the second. The analyser avoids the composition of statistical errors inherent in the calculating of pulse distribution curves from ordinary bias curves, but because only a small fraction of the total number of incoming pulses, lying in the energy band selected, are recorded at each observation, the time taken to cover the whole energy spectrum is considerable and the stability demanded of the amplifier is correspondingly great.

Of the more recent pulse analysers,[194] the majority make use of similar circuit elements to the single-channel model but provide additional channels and recording equipment so that the complete spectrum is scanned in one observation. Amongst the others, one particularly ingenious machine [195] uses an electromagnetically operated cue which strikes a tiny ball-bearing, fed from a reservoir of balls, with a force proportional to the initiating pulse ; the ball describes a trajectory on an inclined table, and runs into one or other of several channels at the bottom of the table. At the conclusion of the observation the histogram of the balls in the various channels corresponds to the pulse size distribution.

In another,[196] the pulse is converted into one of standard height but of duration proportional to the height of the initial pulse. The second pulse gates a stabilized oscillator and the resultant pulses are fed to a sealing circuit. The scaler measures the number of pulses and then triggers one

[193] Roberts, *Rev. Sci. Instr.*, 1940, **11**, 44 ; Frisch, British Atomic Energy Report, 1943.

[194] Sayle, *ibid.*, 1944 ; Poole, *ibid.*, 1944 ; Freundlich, Hincks, and Ozeroff, *Rev. Sci. Instr.*, 1947, **18**, 90 ; Thirion, *Compt. rend.*, 1948, **226**, 706 ; Westcott and Hanna, *Rev. Sci. Instr.*, 1949, **20**, 181 ; Maeder, *Helv. Physica Acta*, 1947, **20**, 139 ; Maeder, Huber, and Stebler, *ibid.*, p. 230 ; Baldinger and Casale, *ibid.*, 1949, **21**, 172 ; Glenn, *Nucleonics*, 1949, **4**, No. 6, 50 ; Ghiorso, Jaffey, Robinson, and Weissbourd, National Nuclear Energy Series, Div. IV, Vol. 14B (McGraw-Hill, 1949, N.Y.), Paper 16.8 ; Kahan and Kwartiroff, *J. Phys. Radium*, 1946, **7**, 300, 357 ; Watkins, *Rev. Sci. Instr.*, 1949, **20**, 495 ; Dexter, U.S. Atomic Energy Commission, A.E.C.D. 2255, Declassified Sept. 1948.

[195] Frisch, *Discovery*, 1948, **9**, 236.

[196] Wilkinson, *Proc. Camb. Phil. Soc.*, 1950, **46**, 508.

of a bank of Post Office counters. Thus the pulse height is coded as a number of pulses, and a scaler is used to determine the number of coded pulses and actuate the appropriate recorder. The apparatus includes a blocking circuit to inactivate the coding circuit until the completion of the recording cycle and to reset the scaler before the next block of coded pulses arrives. This pulse analyser is characterised by greater long-term stability than the previous models and the simpler circuit permits construction of instruments with 100 channels or more. The calibration is linear and the analyser can accept pulses of any shape or time of rise.

Another difficult feature of the disentangling of decay chains was the inadequacy of the methods of detecting and measuring activities of very short half-life. The use of the cathode-ray oscilloscope considerably facilitated these measurements.[197] Another method, in common use to-day, compares the rate of coincidence between the successive nuclear events when different delay times are introduced into the input circuit fed by the initiating event.[198] Several methods of producing delays of a small fraction of a micro-second upwards are known. Such circuit elements were important in the development of radar. Perhaps the most interesting of them is the delay line, consisting of an impedance tapped at regular intervals by condensers, like a low pass filter, with matching elements at each end. Delay lines can be designed to provide delays from a fraction of a micro-second up to several micro-seconds ; the pulse suffers some attenuation but by appropriate choice of impedance and condenser values the delay can be made almost independent of the pulse characteristics.

Collateral Decay Chains.—Several species have already been described that do not lie in the direct line of descent from the heaviest member of the series. These join the chain by β-disintegration or orbital-electron capture ; such isotopes are called collateral members (*e.g.*, ^{233}Th, ^{239}U, ^{229}Pa, etc.). The production of considerably mass-deficient isotopes by bombardment of long-lived species with very energetic ions has shown that decay chains exist that are largely independent of the principal chain. In some cases members may suffer alternative modes of decay which later rejoin the main chain, but some fraction of the disintegrations follow an individual path, involving successive α-particle emissions, and do not connect with the main chain before reaching a polonium or bismuth isotope. Six such collateral chains have been reported. They can be traced in the diagrams on pp. 288–295.

4n Series.—Two collateral chains are known in this series. One comprises isotopes for which $I(=A-2Z)=46$, and is derived [86] from the parent ^{228}Pa formed by ^{232}Th$(d,6n)^{228}$Pa. It joins the main chain at Th-*C*. A recently discovered [199] neptunium isotope, ^{232}Np, produced by ^{235}U$(d,5n)$ for which $I=46$, appears to decay entirely by orbital-electron capture, thereby rejoining the main chain. The main chain bifurcates

[197] Rowlands, *J. Sci. Instr.*, 1948, **25**, 218 ; Schelberg, Sampson, and Mitchell, *Rev. Sci. Instr.*, 1948, **19**, 458.

[198] Bunyan, Lundby, and Walker, *Proc. Physical. Soc.*, 1949, **62**, *A*, 253 ; Van Name, *Physical Rev.*, 1949, **75**, 100.

[199] Magnusson, Thompson, and Seaborg, *ibid.*, 1950, **78**, 363.

above radio-thorium, one branch descending from ^{244}Cm and the other from ^{244}Cf. The collateral members with $I = 50$ do not give rise to a decay chain but all rejoin one or other branch of the main chain.

A second collateral chain descends [200] from ^{232}Pu [^{235}U(α,7n)^{232}Pu], although it was discovered [88] by the production of ^{228}U [Th(α,8n)^{228}U]. These last nuclear reactions are interesting examples of the highly disruptive reactions that have been made possible by the use of the 200 M.e.v. α-particles obtained from the 184″ frequency-modulated Berkeley cyclotron, which began to operate early in 1947. The chain rejoins the natural one at Th-C'. As will be seen from the diagrams, members of both collateral chains exhibit α/K branching.

$4n + 1$ *Series.*—A collateral chain in this series has been found [88] to result from the decay of ^{229}U [^{232}Th(α,7n)^{229}U]. The half-lives of the members of this chain are all short. It rejoins the ^{233}U chain at ^{213}Po.

$4n + 2$ *Series.*—This series also gives rise to two collateral chains. On the other hand, isotopes with $I = 48$ are collateral members of the other chains although some pairs are related by α-disintegration. The chain with $I = 46$ has its origin [147] in ^{238}Cm [^{239}Pu(α,5n)^{238}Cm], although discovered by the synthesis of the collateral member ^{230}Pa. It was the first such chain to be investigated.[84] ^{230}Pa, prepared by ^{232}Th(d,4n)^{230}Pa, is notable in being the only heavy isotope so far reported as disintegrating by both β-decay and orbital-electron capture. The chain joins the uranium decay products at Ra-C' or ^{218}Rn, if Walen's observations are substantiated.[83] Another chain,[88] all of whose members are short-lived, descends from ^{226}Pa [^{232}Th(d,8n)Pa^{226}] through francium and astatine isotopes.

$4n + 3$ *Series.*—The main chain bifurcates at ^{231}Pa, a subsidiary branch descending from ^{243}Bk. One collateral chain[86] has been reported; it descends from ^{231}Np [^{233}U(d,4n)^{231}Np], but was first studied by the decay of ^{227}Pa [^{232}Th(α,9n)^{227}Pa]. The available activities of the parent bodies were in each case very modest, and although the half-lives of most of the decay products were short, the characterisation of these products was essentially dependent on a combination of radiochemical separations with examination of the products by means of the pulse analyser.

Mass-deficient Heavy Nuclei.—A large number of neutron-deficient isotopes of mercury, thallium, lead, bismuth, polonium, and astatine have been prepared.[201] Many of these have been obtained as spallation products from the bombardment of the heavier nuclei. The mercury, thallium, and lead isotopes decay by orbital-electron capture, but some of the astatine, polonium, and bismuth isotopes are α-active. More interesting is the discovery that α-active isotopes of gold and mercury can be obtained by the proton bombardment of gold.[202] The isotopic assignment of these activities has not been determined (they are omitted from the diagrams). It is clear that their mass numbers must be less than 188 and 195 for the gold and mercury isotopes, respectively.

[200] James, Orth, and Seaborg, see Nat. Bur. Stand. Circ. 499.
[201] Templeton, Howland, and Perlman, *Physical Rev.*, 1947, **72**, 755.
[202] Thompson, Ghiorso, Rasmussen, and Seaborg, *ibid.*, 1949, **76**, 1406.

Another region of α-instability lies near mass number 152 amongst the rare-earth elements. Samarium possesses the only naturally α-active isotope in this region. It has recently been found that the bombardment of gadolinium or dysprosium by 200 M.e.v. protons produces α-active isotopes of gadolinium, terbium, dysprosium, and holmium.[203] Our knowledge of nuclear structure is still insufficient to explain the full significance of these observations.

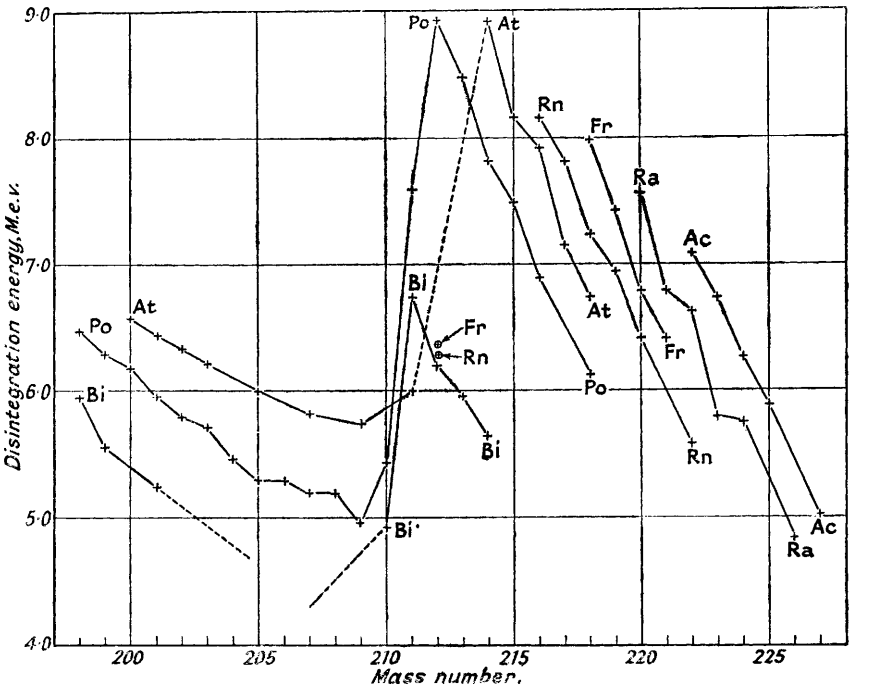


FIG. 5.

Some very light α-active isotopes of francium, radon, and astatine have been discovered amongst the spallation products from the bombardment of thorium with 200 M.e.v. protons. These include ^{212}Fr and ^{212}Rn, together with their decay products ^{208}At and ^{208}Po. The same reaction has been shown to yield ^{210}Rn, ^{211}Fr, and its daughter ^{211}Rn. The last two have so far only been shown to decay by orbital electron capture.

α-Decay Systematics.—The accumulation of empirical data over the last few years has revealed certain regularities in the properties of the α-active nuclei.[204] For instance, the total disintegration energy, that is the sum of

[203] Rasmussen, Reynolds, Thompson, and Ghiorso, *Physical Rev.*, 1950, **80**, 475; Ballou, *ibid.*, 1949, **75**, 1105.

[204] Karlik, *Acta Physica Aust.*, 1948, **2**, 182; Perlman, Ghiorso, and Seaborg, *Physical Rev.*, 1949, **75**, 1096; Wapstra, *Physica*, 1950, **16**, 33.

the α-particle energy, energy of recoiling nucleus, and the γ-ray energy if the daughter nucleus is produced in an excited state, decreases steadily as the mass number increases for each element beyond radium. For polonium, on the other hand, the disintegration energy at first rises steadily as the mass number decreases until ^{212}Po is reached; it then falls very sharply to ^{209}Po, when it again begins to rise rather more slowly than before [205] (see Fig. 5). The bismuth, astatine, radon, and francium curves show similar characteristics although the data are very incomplete for the last two elements, depending largely on the recently discovered light isotopes. For these elements, the maximum α-energy appears for nuclei with about 128 neutrons and the minimum at about 126 neutrons. The latter number is one of the so called "magic" numbers,[206] which an empirical study of nuclear stability associates with the completion of different nuclear quantum levels. The α-active rare earths are clustered near an analogous "magic" number of 82 neutrons. It will be seen that the astatine curve provides a minimum α-energy for the isotopes of this element and thus sets a limit to the longest-lived isotope of the element that can be expected.

A more detailed examination of the theory of α-decay has become possible by using these extensive new data. The one-body model of α-decay appears to fit the even–even nuclei (Z even, A even) rather well, but the other nuclei generally decay rather more slowly than this theory requires, suggesting that time is needed for the assembly of the α-particle within the nucleus. The nuclei with about 126 neutrons also show anomalous properties suggestive of a sharp contraction in nuclear radius amounting to some 8% for ^{210}Po.

[205] Perlman, Ghiorso, and Seaborg, *Physical Rev.*, 1950, **77**, 26.

[206] Meyer, *ibid.*, 1948, **74**, 235; 1949, **75**, 1969; Brightsen, *Nucleonics*, 1950, **6**, No. 4, 14.