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NATURAL RADIOACTIVITY OF THE HEAVY ELEMENTS:
A COMPREHENSIVE REVIEW

Earl K. Hyde

Author's note: This report is part of a larger work dealing with the nuclear properties of the heavy elements, which accounts for the peculiarities in the numbering of tables, figures and report sections. It is a self-contained review and should prove useful apart from the rest of the material with which it will ultimately be published. The literature was searched up to September 1962. The author will be grateful for notice of important errors, omissions or misinterpretations.
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NATURAL RADIOACTIVITY OF THE HEAVY ELEMENTS:
A COMPREHENSIVE REVIEW

This review describes the three heavy-element families of radioelements which occur in nature. It begins with an account of the early history of radioactivity. This was one of the most fascinating periods in the whole history of science and in our account we attempt to show how the experiments designed to explore this strange new phenomenon of radioactivity and to unravel the confusing genetic relationships of the radioelements stimulated the formulation of bold new ideas on the nature of radioactivity and on the fundamental composition of the atom.
6.1 EARLY HISTORY OF RADIOACTIVITY

Becquerel's Discovery of the Radioactivity of Uranium. The discovery of radioactivity followed within a few months of the announcement of Röntgen's mysterious x-rays and was the direct but unexpected result of some experiments designed to clarify some of the phenomena described by Röntgen. It had been observed that x-rays were emitted from those parts of the glass wall of the discharge tube which were bombarded with cathode rays. It had also been observed that the bombarded parts of the glass wall emitted a greenish or bluish fluorescence. Professor HENRI BECQUEREL immediately interested himself in the question whether certain materials rendered fluorescent or phosphorescent by light also emitted radiations analogous to x-rays.

BECQUEREL had been interested in fluorescence for some years following a family tradition going back to his grandfather. In particular, he had on hand a compound of uranium - a double sulfate of uranium and potassium - which he had prepared fifteen years before and which he had observed to fluoresce brilliantly under ultraviolet light. He placed two samples of this double salt upon a photographic plate wrapped in black paper. Between the black paper and one of the salt samples he placed a coin. Knowing that an excitation by sunlight was necessary to excite the phosphorescence and believing that such excitation would be required for any other radiations, he exposed the combinations of wrapped photographic plate and uranium compounds to the sun. After an exposure of several hours, he developed the plate and observed a light image of the uranium samples and the shadow produced by the piece of money. These first experiments gave the expected results and did not lead to any important discovery.

BECQUEREL then proceeded to a study of the penetration of the new radiations through various thicknesses of absorber, always placing his uranium salts in the sun during the exposure of the plate. On February 26, 1896, he had prepared such a set of experiments but was prevented from completing them by poor weather which obscured the sun. The experimental preparations consisting of the photographic plates, the absorbers and the

*Throughout Section 6.1 names of investigators are given without references to published literature.
double salts of uranium and potassium were placed in a drawer for a several
day period. On March 1, the sun reappeared and BECQUEREL prepared to resume
his experiments. He was somewhat uneasy about using his several-day old
preparations which had been exposed to a little sunlight before being stored
in the darkness and he decided to replace the plates with new ones. In this
way he could be quite certain that the experimental conditions were identical
with those of previous experiments. In addition, he decided to see whether
the withdrawn plates had indeed received some exposure and dropped them into
a developer bath. He expected to see very light impressions or none at all
and was astonished to observe silhouettes of the uranium salts which were of
much greater intensity than in any of his previous experiments! Exposure to
sunlight evidently was not essential to the emission of the penetrating
radiation. The date of this observation, which was March 1, 1896, may be
taken as the birthdate of radioactivity.*

Further experiments revealed that the effect on the photographic plate was not related to the ability of uranium compounds to fluoresce and
in fact that any uranium salt would produce the effect. Furthermore the
strength of the photographic images under identical conditions of exposure
was directly proportional to the atomic content of uranium in the preparation.
HENRI BECQUEREL concluded that the new property was to be associated with
the uranium atom and did not depend upon its state of chemical combination.

Thus it came about that the penetrating radiations emitted by radioactive bodies were first noticed and called to the attention of the scientific world.

Discovery of Radioactivity of Thorium. Immediately after the dis­
covezy of the radioactivity of uranium, a large number of elements were
tested for radioactivity using an electroscope as the detection method. The
only other element found to be radioactive was thorium. Its activity was
found independently by G. C. SCHMIDT and by MADAME CURIE in 1898.

Discovery of Polonium and Radium. The experiments of BECQUEREL and
others had established that the amount of radioactivity in any uranium com­
pound was directly proportional to the uranium content. Hence it came as a
considerable surprise when measurement of the radioactivity of certain pitch-

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*Henri Becquerel himself used the term "activite radiante". The word radioactivity, adopted later, was proposed by Marie Curie.
blende ores gave values about 4 times greater than expected on the basis of the uranium content. (Mme. CURIE, 1898). Mme. and P. CURIE decided that this could be so only if pitchblende contained small quantities of an element or elements of greater specific activity than uranium or thorium. With this hypothesis as a basis the CURIES carried through a systematic fractionation of the ore, using the radioactivity of the various fractions as a guide and discovered during the year 1898 the two unknown elements polonium and radium.

Polonium was the first of the active substances to be obtained from pitchblende. A bismuth fraction isolated by precipitation of bismuth sulfide removed the new element from the bulk of the pitchblende ore. Further purification was carried out by partial precipitation of the subnitrate of bismuth by diluting nitric acid solutions of the mixture. No completely satisfactory method for the preparation of chemically pure polonium was developed in these early years. MARCKWALD removed polonium from a bismuth chloride solution obtained from uranium residues by dipping a rod of bismuth metal into the active solution. Polonium (and considerable inert tellurium impurity) electrodeposited on the bismuth metal surface. MARCKWALD believed his activity was different from Mille... CURIE'S polonium and for some time referred to his substance as radio-tellurium.

The radiations of polonium were observed to differ in important respects from the radiations of uranium or radium. Only the heavily-ionizing short-range alpha rays were observed and no beta or gamma radiation was detected. Furthermore the activity decreased in time so that over a period of about 140 days, half the activity disappeared. One explanation for this decreasing activity which enjoyed a certain vogue for a time was that polonium was not a new active substance but merely bismuth in which radioactivity had somehow been "induced" by admixture with radioactive bodies. A third important particular in which the activity of polonium differed from uranium was that the specific activity of partially-purified samples was enormously greater than that of uranium.

Shortly after the discovery of polonium a second extraordinarily active body was isolated from pitchblende by the CURIES (1898). This substance was radium. Radium is a heavy homologue of barium and resembles it closely in chemical properties. Considerable barium is present in pitchblende and when it is isolated from the other elements found in the ore, the radium is isolated
with it. To separate radium from barium the CURIEs employed the method of fractional crystallization. Fractional crystallization of mixtures of barium and radium chloride from water, or from alcoholic or hydrochloric acid solution resulted in the desired separation. Since radium chloride is less soluble, it is enriched in the crystal phase and after a large number of recrystallizations it is possible to prepare radium almost completely free of barium. GIESEL found that fractional crystallization of the bromide was more effective than fractional crystallization of the chloride. The amount of radium in pitchblende is quite small and several tons of pitchblende must be worked up to obtain a few hundred milligrams of radium. Hence the labor involved in these early researches was very great.

The extent of the separation was followed by determining the specific activity of the radium which eventually reached a value more than a millionfold greater than that of uranium.

A number of experimental studies were performed to determine beyond question that radium was a true chemical element with unique properties in addition to its intense radioactivity. The emission spectrum of radium was measured by DEMARCA Y and shown to consist of characteristic lines similar to those of the alkaline earths. In its chemical properties it was found that radium forms a series of compounds similar to barium. Radium metal was prepared by Mme. CURIE and DEBIERNE in 1910.

The atomic weight of radium was determined by Mme. CURIE in 1902 by weighing a 90 milligram sample of radium chloride and determining the chloride content by precipitation and weighing of silver chloride. The purity of the radium, with particular emphasis on barium content, was determined spectroscopically. The value of the atomic weight was 225.2. Mme. CURIE repeated her work in 1907 with 400-milligram samples of radium chloride and obtained the value 226.45. A very careful series of determinations was carried out by HÖNIGSCHMID in 1911 using samples of radium chloride as large as 680 milligrams. HÖNIGSCHMID'S value of the atomic weight was 225.95 based on the value 107.88 for silver and 35.457 for chlorine.

The determination of the atomic weight and of the distinctive physical and chemical properties of radium fixed its location in the periodic chart in the eka-barium position. This knowledge served as a valuable reference point in the assignment of other members of the uranium-radium decay chain
as they were discovered later. For many years, except for uranium and thorium, the atomic weight of no other radioactive element was known. The placement of actinium and of its decay products in the periodic system, for example, was uncertain for decades because it was not isolated in sufficient purity to permit an exact determination of its atomic weight.

**Discovery of Actinium.** Dr. DEBIERNE assisted the CURIES in their early studies of the radioactive substances present in pitchblende by supervising the large scale crude fractionation of pitchblende residues. In 1899 while engaged in this work, he discovered a new activity which followed the iron group of metals in the fractionation. He called this substance actinium and stated that it was very similar to thorium in its chemical properties. In 1900-1902 GIESEL reported the discovery of another active substance from pitchblende which he called "emanium" because it emitted a short-lived emanation, GIESEL showed that his substance was similar in chemical properties to the rare earths. It was later concluded that GIESEL'S "emanium" was identical with DEBIERNE'S actinium and the name "emanium" was dropped.

**Radiolead.** HOFFMAN and STRAUSS in 1901 concluded that the radioactivity observed in a lead fraction removed from pitchblende was due to a new substance which they called radio-lead. The identification of this activity with radium D came some years later.

**The Radioactive Emanations.** Before 1900 it was observed that radium, thorium, and actinium continuously emit into the surrounding space a material emanation with the properties of a radioactive gas. This emanation diffused in a current of air, and diffused through paper, plugs of glass wool and other porous materials. It could be pumped away and condensed at a low temperature. The first emanation to be discovered was the 54-second thoron produced in samples of thorium. It was at first presumed that thoron was a direct result of the disintegration of thorium but RUTHERFORD and SODDY in 1902 showed that thoron was in actuality a decay product of ThX, an intermediate product.

The first report of the existence of radon is credited to DORN. He found that a small amount of radioactive gas was released by radium preparations at ordinary temperatures but that much more was released if the radium was heated or dissolved. The first attempt to measure the rate of.
decay of radon was carried out by P. CURIE who obtained a half-life of 3.71 days in 1902. RUTHERFORD and SODDY reported a value of 3.99 days in 1903. Careful measurements by Mme. CURIE in 1910 and by RUTHERFORD in 1911 gave 3.85 days.

GIESEL in 1903 found that actinium gives out an emanation which has a much greater rate of decay than thoron or radon. The emanation later received the name actinon.

Because the short half-lives of thoron and actinon made them difficult to study, radon received much more attention. Radon was subjected to very severe chemical treatments to see whether its properties could be changed. It was found that it showed a truly remarkable chemical inertness and retained its gaseous nature throughout. The only known elements possessing these properties were the then recently discovered members of the argon family of rare gases. (RAMSAY). It was found that radon (and thoron) could be condensed at low temperatures. Some detailed experiments of RUTHERFORD and SODDY in 1903 placed the condensation temperature at -150°C. The first measurement of the atomic weight of radon was carried out by GRAY and RAMSAY in 1911. Using a remarkably sensitive quartz microbalance these experimenters measured gas samples weighing less than one microgram and determined a value of 223 for the mass number. The emission spectrum of radon was observed by a number of investigators in the period 1908-1909.

Nature of the Radiations. Radioactivity was detected and measured by three methods in this early period; the photographic method, the "electric" method and the excitation of fluorescence in fluorescent materials. Photographic plate detection was particularly useful for β and γ detection. The "electric method" was based on the ionization caused in a gas volume by passage of the radiations and was particularly useful for alpha particles. A number of sensitive electrometers and electroscopes were developed for this purpose. Fluorescent materials such as barium platinocyanide and zinc sulfide were found to be useful chiefly for alpha radiation. The spinthariscope, consisting of a low power magnifier focused on a screen of zinc sulfide, was developed to count individual alpha particles. In 1911 C. T. R. WILSON introduced the expansion cloud chamber for observing the tracks of individual γ, α or β rays.
RUTHERFORD in 1899 distinguished two kinds of rays coming from uranium differing greatly in penetrating power; he called these the α- and β-rays. Alpha-rays are readily absorbed by the absorber foils, but are heavily ionizing throughout their range. Beta-rays are far more penetrating than α-rays but have much less ionizing power. Later a third type of ray even more penetrating than the β-rays was discovered by VILLARD and these were name γ rays. An important advance in the understanding of the nature of the radiations came in 1899 when several laboratories independently observed the deflection of the β-rays in a magnetic field. Quantitative measurements of the deflection in magnetic and electric fields showed that beta-rays were negatively charged particles with the same e/m as cathode rays. Beta particles were identified as electrons moving with velocities approaching the speed of light. The inhomogeneity in energy of the beta-rays was also well established by 1900, but many years were to pass before a clear distinction between beta-rays and conversion electrons would be made.

Approximately three years passed before the deflectability of the alpha radiations in magnetic and electric fields was established because of the much greater difficulty of deflecting the alpha-rays. STRUTT in 1901 first suggested that alpha-rays might consist of rapidly moving positively charged bodies similar to the canal rays produced in a vacuum tube. Similar proposals were made by CROOKS, Mme. CURIE, and RUTHERFORD. RUTHERFORD first showed the deflection of the alpha rays in a magnetic and an electric field. The deflection was in the direction expected of positively charged particles and the value of e/m derived from the measurements correspond to a particle of mass similar to hydrogen or helium. For some time it was supposed that the charge on the alpha particle was one electronic charge and that the mass was twice that of the hydrogen ion. In 1908 RUTHERFORD and GEIGER established that the electronic charge on the alpha particle was two units, which made the mass of the alpha particle identical with an atom of helium.

RUTHERFORD and SODDY suggested in 1902 that helium might prove to be a disintegration product of radioactive materials. Helium had been found in the spectrum of the sun in 1868 but only in 1895 had helium been found to exist on the earth. It was noteworthy that helium was found in considerable quantity in minerals containing uranium and thorium; the presence
of such a light gas as helium in such minerals was an unusual fact, particularly since none had been found in non-radioactive materials.

A key experiment was carried out by Ramsay and Soddy in 1903. These investigators obtained direct evidence that helium was formed in the disintegration of radium. Thirty milligrams of radium bromide purified three months previously was dissolved in a closed system. The evolved hydrogen and oxygen were removed by recombining them to form water. Spectrum analysis of the residual gas not condensed in liquid air showed the characteristic $D_3$ line of helium. Subsequent experiments in several laboratories verified the production of helium in the decay of actinium, polonium, ionium and other alpha-emitting materials. Quantitative measurement of the small helium gas volumes showed that the rate of helium production was that to be expected from the rate of emission of alpha particles. In 1908 Rutherford and Royd extended these experiments in an important way by pumping an intense sample of radium emanation into a thin-walled glass tube, and collecting and identifying as helium the gas which emerged through this thin glass tube into a surrounding evacuated space. Tests were made to prove that ordinary helium could not diffuse through the thin wall. On the other hand the energetic alpha particles could penetrate the glass. This experiment even more clearly identified the alpha particles as rapidly-moving ions of helium.

In distinction from the alpha and beta radiations the gamma radiation could not be deflected by electric or magnetic fields. It was shown to be similar to the x-radiation produced in vacuum tubes but of considerably shorter wave length.

A great deal of attention was devoted to the study of the absorption and scattering of the $\alpha$, $\beta$ and $\gamma$ rays. We shall not review these studies in this historical account except to discuss some properties of alpha rays which had a very marked influence on the development of radioactivity.

Concept of Alpha Particle Range. Let us first discuss the development of the concept of alpha range. Mme. Curie made measurements on thin samples of polonium shortly after her discovery of this element which showed that the ionization caused by the alpha rays ceased suddenly after traversing a definite thickness of air or other absorber. This was a markedly different behavior from gamma radiation of x-radiation which was absorbed according to an exponential law.
When it began to be clear that alpha rays were positively charged atoms moving with very high velocities, BRAGG put forth the view that each alpha particle traveled in nearly a straight line, expending energy in ionization until its velocity was reduced below a certain value. According to his view each alpha particle should have a definite range of travel. Experiment showed that each alpha emitter emitted particles with a characteristic range, usually expressed in centimeters of air at atmospheric pressure and 15°C. From this time forth the determination of the range of the alpha particles emitted by a new radioelement was an important step in deciding whether it was actually different from previously known radioelements.

When the range of the alpha particles had been measured for a large number of radioelements it was observed that there appeared to be a connection between the half-life of a product and the velocity of the alpha-particles. The shorter half-lives were associated with the more energetic alpha emitters. This was formulated quantitatively in the relationship of GEIGER and NUTTALL (1911-1912) who found that the alpha-emitters of a given series fell on a straight line if the logarithm of the range was plotted against the logarithm of the half-life. This relationship had a practical usefulness in making it possible to estimate the half-lives of certain radioelements when the alpha particle range was known, but the half-life could not be measured directly. The half-life of uranium II (U$^{234}$), for example, was estimated to be about $10^6$ years from the observed range of the alpha particles. This was the only way in which the half-life of this isotope could be estimated until A.O. NIER measured the isotopic composition of natural uranium in 1939.

The Rutherford Nuclear Model of the Atom. Another outcome of the study of the detailed properties of alpha particles which had the utmost importance for the development of radioactivity and of all nuclear physics was the formulation of the RUTHERFORD model of the atom. GEIGER and MARDEN observed in 1909 that when a beam of alpha particles impinged on a thin sheet of matter, most of the particles were scattered only a few degrees or less from their incident direction. Some, however, changed their direction sharply, in some cases to the extent that they were scattered backwards from the foil. The number which were scattered through large angles, while small, was too large to be explained by multiple scattering or by single scattering by the most intense electrical potential (of the order of 100,000 electron volts).
supposed to exist within the atom according to the THOMSON model of the atom in favor at that time.

To explain the anomalous scattering RUTHERFORD proposed (1911) his brilliant theory of the nuclear atom. In order to explain an intense electrical field within the atom RUTHERFORD proposed that the positive charge was concentrated into a very small central region which he termed the nucleus and that the compensating negative charge is distributed over a sphere whose radius is identifiable with the radius of an atom. Using this atomic model RUTHERFORD calculated quantitatively the expected distribution of scattered alpha particles. This distribution in all its particulars was verified later (1913) by the meticulous experiments of GEIGER and MARSDEN.

A few years later in a series of papers published during the period 1913-1915 NIELS BOHR used the Rutherford nuclear atom and the quantum theory of radiation as developed by PLANCK and EINSTEIN to develop the quantum theory of atomic structure which came to be known as the Bohr-Rutherford atom. This model of the atom had its most sweeping success in the explanation of atomic spectra and atomic phenomena but it also had very great importance in making understandable many of the main features of radioactive decay.

An important element of the Rutherford nuclear atom was the charge number \( Z \) to be associated with the nucleus. The identification of this number with atomic number was not at all clear until the work of MOSELEY appeared during 1913-1914. MOSELEY made a systematic study of the wavelengths of the K series and L series of x-rays which were emitted by the elements when bombarded with cathode rays. He noted that there was a regular change in the wave length of each series when the elements were arranged in the order of their position in the periodic table. The extreme regularities which he noted could be explained only if there was a very regular change in some quantity within the atom in going from one element to the next heavier element; he concluded that this quantity was the positive charge on the nucleus. MOSELEY concluded that the number of unit positive charges on the nucleus is the same as the number of the place occupied by the element in the periodic system; this number he called the atomic number. The atomic number immediately replaced the atomic mass number as the fundamental quantity to be associated with any element.
In the region of the radioactive elements it was recognized that the atomic number of uranium was 92, of thorium 90, etc. When the atomic number concept of MOSELEY and the Rutherford Nuclear Atom were used in connection with the SODDY isotope conception and the displacement laws of radioactivity it was possible at once to write down in simple and understandable form nearly the entire sequence of radioactive decay for the three naturally-occurring series. It is necessary to recognize, however, that during the first decade and a half of intensive investigation of the radioelements initiated by BECQUEREL'S discovery these theories were unknown. The nature of each new radioelement had to be deduced from its chemical and physical behavior and its genetic relationship to other radioelements. By 1913, 32 separate radioactive species had been discovered and studied.

Energy Release and the Nature of Radioactivity. Immediately after the first studies of radioactivity, it was pointed out that the total energy represented by these energetic radiations was enormously greater than for any known chemical process. Furthermore the rate of energy emission was totally uninfluenced by variation in temperature, pressure, by chemical form, or by any other physical or chemical factor which causes changes in ordinary chemical reactions. The first direct measurements of the heat emitted by radium, carried out by P. CURIE and LABORDE in 1903, showed that one gram of radium emits about 100 gram calories of heat per hour and that this large heat emission apparently had continued for centuries.

The many suggestions put forward to explain this large store of energy could be divided into two broad groups. According to one set of views the radioactive elements possessed some peculiar property enabling them to extract heat from their surroundings or from unknown radiations impinging on all matter and to convert the energy so abstracted into the form of $\alpha$, $\beta$ and $\gamma$ rays. The second view was that radioactivity in some ways involved the breakup of the atom and the ejection of part of the atomic system and that this process released large amounts of potential energy residing in the atom. The material nature of the $\alpha$ and $\beta$ rays supported this view. It was impossible to formulate any detailed theory since at that time nothing was known about the structure of the atom or of a distinction between the atomic nucleus and the extra-nuclear electrons. The picture of the atom current at that time followed the ideas of J. J. THOMSON, (and of
Larmor and Lorentz and of Kelvin) who conceived of the atom as a sphere containing positive and negative particles distributed in some regular fashion throughout and held in equilibrium by electrical forces.

**The Rutherford-Soddy Theory of Radioactivity.** The discovery of the radioactive emanations and the isolation of other short-lived radioactive elements from vessels or from solutions in which the long-lived radioactive elements such as radium had been allowed to remain provided valuable clues to the true nature of the radioactive transformations. These clues led to the theory of radioactivity put forward by Rutherford and Soddy in 1902. The observations which were particularly illuminating were those connected with the discovery of the substances given the names Uranium X and Thorium X.

In 1900 Sir William Crookes showed that the source of the beta radiation associated with uranium could be isolated from uranium in a single chemical operation. If uranium were precipitated as the carbonate and then dissolved in an excess of ammonium carbonate, a residue of impurity elements remained behind and with this residue remained all the beta activity. This activity was called uranium X. The alpha radiation as measured by the electrical method remained entirely with the uranium. Becquerel showed that this uranium X activity could be removed from uranium solution by precipitation of barium sulfate. The inactive uranium and the active barium were laid aside. They were re-examined a year later and the surprising fact was found that the uranium had regained its activity while the barium sulfate had become completely inactive.

Similarly in the case of thorium, Rutherford and Soddy found that an active constituent, named by them thorium X (ThX), could be found in solution when thorium was precipitated with ammonia. The specific activity of the ThX was several thousandfold greater than that of the thorium. Within a period of a month the thorium regained its activity while the ThX became quite inactive.

The time rate of these processes of decay and recovery of activity was studied and curves such as that shown in Fig. 6.1 were obtained.

Consideration of these phenomena led Rutherford and Soddy to formulate their famous theory of radioactive decay. According to this theory (1) there is a constant production of fresh radioactive matter by the decay of another radioactive body and (2) the activity of the matter so formed decreases
Fig. 6.1. Decay of beta-activity in ThX (3.64 day $^{224}$Ra) freshly separated from thorium and the regrowth of activity into the thorium.
according to an exponential law from the moment of its formation. The daughter radioactive matter has chemical properties distinctly different from its parent and can be isolated chemically from it. When such a separation is made the daughter activity decays in an exponential fashion with a decay constant characteristic of that particular radioactive element; the rate of this decay is uninfluenced by any external condition. The regrowth of the daughter activity into the separated parent also occurs at a characteristic rate uninfluenced by external conditions. In an undisturbed sample the amount of daughter activity reaches an equilibrium amount when the rate of disintegration of the matter already in the sample is just balanced by the matter supplied by the production of new matter.

To explain the differing chemical properties of the parent and descendental radioactivities it was postulated by RUTHERFORD and SODDY in 1903 that radioactive decay was an atomic phenomenon. Atoms of some elements possess a fundamental instability and on the average a constant small percentage of them break up every second by expelling one or more material particles—α or β rays—with great velocity. The part of the atom left behind has different chemical properties. It is possible that these new atoms are also not permanently stable and that a certain percentage of them will break up each second.

According to the RUTHERFORD and SODDY theory it was important that the characteristic disintegration constant, λ, or some quantity related to it such as the half-life \( T_{1/2} = \frac{0.693}{\lambda} \) be determined for each radioactive element. In the case of uranium X the half-life was easily determined to be 24.6 days corresponding to a disintegration constant \( \lambda = 0.0288 \text{ days}^{-1} \). In the case of thorium X the half-life was determined to be 3.65 days corresponding to a disintegration constant of \( \lambda = 0.190 \text{ days}^{-1} \).

The disintegration theory was applicable to any series of genetically related radioelements. The logarithmic law of radioactivity is very simple when a single activity is considered. However, when a series of several genetically related radioelements is considered the changes in the amount of an individual product or of the gross activity can be quite complex. RUTHERFORD deduced the general mathematical expressions applicable to the major types of decay chains observed in practice. This mathematical development was a very powerful tool in unraveling the chain of radioactive transformations.
represented by the active deposits left by the radioactive emanations. It was used constantly in deciding on the relationship of any newly discovered radioactive element to those already known.

The Active Deposits. P. and Mme. CURIE in 1899 noted that any substance placed in the neighborhood of a radium preparation behaved as if its surface were covered with an invisible deposit of intensely radioactive matter. This activity became known as "induced" or "excited" radioactivity. RUTHERFORD independently noted the same phenomenon for thorium preparations. It soon became established that this activity was intimately related to the emanations of radium and thorium and that it consisted of non-gaseous radioactive products produced by the disintegration of the gaseous emanations. The term "induced activity" was dropped in favor of the more suitable "active deposit."

It was found that the active deposit could be highly concentrated on negatively charged metal wires or surfaces placed in closed vessels containing the emanation. Such wires or foils gave convenient sources for study of the radiations because the activity was highly concentrated and essentially weightless. It was found that treatment of the surface with acids would remove the radioactive deposit from the wire. In this case the radioactivity was presented in the acid solution and its chemical properties could be studied.

The Active Deposit from Thoron. The active deposit left by the decay of thoron, radon, or actinon is not a simple activity but a mixture of activities. In the case of the thoron active deposit it was ultimately determined that the sequence of products was the following:
The first product, ThA, is so short-lived that special methods are required to measure it. MOSELEY and FAJANS first determined (1911) the half-life of ThA by collecting it on a rapidly-rotating, negatively-charged metal disc as it was formed from the decay of the thoron. The activity of the matter so deposited was examined at different angular distances from the point of deposit. They determined in this way a half-life of 0.14 sec, which is quite close to the value presently accepted. MOSELEY and FAJANS applied this same method to the first product in the active deposit of actinon and found a half-life of .002 seconds for AcA. This was the shortest half-life known for any radioactive element at that time.

The controlling activity in the active deposit of thoron is ThB which decays with a half-life of 10.6 hours. Further details on the active deposit of thoron will be presented later when the various members of the naturally-occurring decay chain are discussed separately.

The Active Deposit from Radon. The active deposit left on surfaces exposed to radon shows a complex decay. The transformation sequence can be divided into a preliminary sequence of rapid change involving the activities with the designation RaA, RaB, RaC, RaC', and RaC" and a final sequence of very slow change composed of the activities RaD, RaE and RaF. These products will be discussed systematically in the next section.
Main Decay Sequence of the Active Deposit of Radon

\[
\begin{align*}
\text{Po}^{218}_{\text{(RaA)}} & \xrightarrow{\alpha 3.05 \text{ min}} \text{Pb}^{214}_{\text{(RaB)}} \xrightarrow{\beta 26.8 \text{ min}} \text{Bi}^{214}_{\text{(RaC)}} \xrightarrow{\beta 19.7 \text{ min}} \\
\text{Po}^{214}_{\text{(RaC')}} & \xrightarrow{\alpha 1.5 \times 10^{-4} \text{ sec}} \text{Pb}^{210}_{\text{(RaD)}} \xrightarrow{\beta 19.4 \text{ yr}} \text{Bi}^{210}_{\text{(RaE)}} \xrightarrow{\beta 5.0 \text{ d}} \\
\text{Pd}^{210}_{\text{(RaF)}} & \xrightarrow{\alpha 138 \text{ d}} \text{Pb}^{206}_{\text{(RaG)}} \text{ Stable}.
\end{align*}
\]

It would take us too far afield to discuss in detail the interesting detective work involved in unraveling the course of this decay sequence but a few points may be mentioned. One approach to the problem was to follow the decay of the active deposit starting immediately after removal of the emanation and to deduce the half-lives of the successive products by the shape of the observed curves using the mathematical relations derived by RUTHERFORD. The analysis was difficult because the shape of the decay curve was dependent on the length of time of exposure to emanation and because the alpha emitting products were detected so much more efficiently than the beta emitting products. Nevertheless it was concluded that the first three changes consisted of Radium A decaying by alpha particle emission with a half-life of 3 minutes, Radium B, a rayless product decaying with a half-life of 21 minutes and Radium C, decaying with a half-life of 28 minutes and emitting \(\alpha, \beta\) and \(\gamma\) rays. The separation of Radium B from Radium C was carried out by BRONSON (1905) by volatilizing the Radium B (a lead isotope) from Radium C (a bismuth isotope). VON LERCH (1906) showed that Radium C could be obtained in a pure state by contacting a foil of nickel with a solution of the active deposit.

The Recoil Collection Method. Somewhat later (1909) the recoil collection method for the separation of radioactive daughter products was introduced by HAHN and by RUSS and MAKOWER. The general method consists of placing a negatively-charged collector plate quite near to a plate covered with active material. During radioactive decay the daughter atom is given enough momentum to balance the momentum of the ejected \(\alpha\) or \(\beta\) ray. This may be sufficient to eject it from the surface of the original active plate,
and since the daughter atom is left positively charged during the decay process it will be accelerated toward the collector plate. This process can be quite effective for the daughter products of energetic alpha emitting parents. It is much less prominent for daughter atoms of beta-emitting parents because of the much smaller recoil momentum. RUTHERFORD had previously calculated the recoil momenta to be expected from alpha and beta processes.

Pure samples of 26.8-minute RaB could be obtained in high yield by this method using the 3-minute alpha-emitter RaA as the source activity. Pure samples of RaC could be obtained from the beta-emitter RaB, but the collection efficiency was only about 1/6000.

The recoil method is of very general applicability and was an important aid in determining the course of the decay chains. It helped to determine the direct parent-daughter relationship of two activities in several instances. It also aided in the discovery of quite short-lived products which had been missed. For example the recoil method was instrumental in showing that Radium C was a complex activity decaying by two paths. The work of HAHN and MEITNER (1909) and FAJANS (1911) showed that a product which they called Radium C₂ (later relabeled RaC") was produced in a very small percentage of the disintegrations. This product showed a half-life of 1.38 minutes. The main decay resulted in the direct production of Radium D (actually years later it was found that the short-lived alpha emitter RaC' occurred between RaC and RaD). The discovery of Radium C₂ was important because it was the first instance in which definite evidence was presented for branching decay. Later several instances of branching decay were verified.

The active deposit observed on bodies which have been exposed to radon gas decreases to a very low level within a day's time after removal of the radon but does not decrease to zero. The residual activity, known as the active-deposit-of-slow-transformation consists of Radium D, Radium E and Radium F. Radium D, a slowly decaying substance emitting soft β rays, was found to be identical with the "radio-lead" separated earlier by HOFFMANN and STRAUSS from uranium minerals. The half-life of RaD was too long to determine by direct counting methods and was determined indirectly by an application of the RUTHERFORD and SODDY disintegration hypothesis. RUTHERFORD in 1904 estimated a value of 40 years; ST. MEYER and SCHWEIDLER
in 1907 estimated 37.5 years. ANTONOFF in 1910 determined a value of 16.5 years which is rather close for such a difficult measurement to the presently-accepted value of 19.4 years.

Radium E is a 5-day activity emitting high energy beta rays. It can be separated from Radium D or Radium F by deposition on a nickel plate.

Radium F was shown to be an alpha emitter identical with the element polonium which Mme. CURIE had isolated from pitchblende. Radium F has the important property that its transformation product shows no radioactivity. Hence it was deduced that the chain of radioactive changes initiated by radium comes to an end at this stage.

The Active Deposit From Actinon. The active deposit from actinon is now known to go through the sequence shown here. We have mentioned how

**Decay Sequence of the Active Deposit of Actinon**

\[ \text{AcA (Po}^{215} \) \xrightarrow{\alpha \text{, } 1.83 \times 10^{-3} \text{ sec}} \text{AcB (Pb}^{211} \) \xrightarrow{\beta \text{, } 36 \text{ min}} \text{AcC (Bi}^{211} \) 2.16 \text{ min} \]

\[ \text{AcB (Pb}^{211} \) \xrightarrow{\beta} \text{AcC (Bi}^{211} \) 2.16 \text{ min} \]

\[ \text{AcC (Bi}^{211} \) \xrightarrow{\alpha \text{, } 0.005 \text{ sec}} \text{AcD (Pb}^{207} \) \xrightarrow{\beta \text{, } 4.76 \text{ min}} \text{Stable} \]

MOSELEY and FAJANS (1911) used the method based on recoil collection of AcA on a rapidly revolving disc to measure the very short half-life of Actinium A. They reported a value of .002 seconds. The course of the transformation of AcB through a series of products to the stable end-product Actinium D was determined through the contributions of many investigators. Analysis of the decay curves of the mixture, and separation of individual products by volatilization, by electrodeposition, or by recoil collection aided in the assignments.
Ionium. The discovery of ionium had an interesting history. It was an outcome of a search for a radioactive parent of the element radium. Consideration of the relatively short half-life of radium and of the RUTHERFORD-SODDY transformation theory led to the conclusion that radium must be continuously replenished in radioactive minerals by some longer-lived precursor. The constancy of the ratio between radium and uranium in minerals suggested that uranium was the parent of radium. However, if this were the case, radium should grow back at a readily detectable rate into purified uranium samples, and experimental checks showed that the regrowth of radium was more than one thousandfold less rapid than would be predicted. It was necessary to postulate a relatively long-lived intermediate between uranium and radium.

BOLTWOOD (1906) proceeded to search for this missing intermediate and during some experiments with the mineral carnotite isolated a preparation which he at first believed to be actinium. BOLTWOOD kept his "actinium" preparation in a sealed bulb and periodically tested it for radium content by measuring the radon gas content. He observed that radium was growing into his sample and concluded that actinium was the parent of radium. To confuse the situation further RUTHERFORD obtained a sample of actinium from GIESEL, who had discovered actinium in 1902 almost simultaneously with DEBIERNE, and found that radium rapidly grew into this preparation too. This was caused by a considerable ionium impurity in GIESEL'S actinium sample. BOLTWOOD (1907) re-examined his original preparation and found it was not actinium but a new substance which he called ionium. By separating ionium from a number of minerals, he found that the rate of production of radium was directly proportional to the amount of ionium. The experiments of BOLTWOOD, OF KEETMAN, and of AUER V. WEISBACH showed that ionium was identical in its chemical properties to thorium and could not be separated from thorium. This made it difficult to measure the half-life of ionium by specific activity measurements but various lines of evidence served to bracket the half-life in the range of 100,000 years.

Uranium 2 (Uranium II). With the discovery of ionium it was possible about 1910 to write the uranium decay chain as follows:

Uranium → Uranium X → Ionium → Radium → Radium Emanation → Active Deposit.
The fact that uranium itself is not simple but must contain two alpha emitting substances was deduced from a very simple experimental fact. In the decay chain of uranium as understood at the time were six products which emitted alpha particles. According to this the number of alpha particles emitted by a thin deposit of an uranium ore in equilibrium with its descendants should be just seven times that of an equivalent amount of pure uranium. Instead, it was found that the mineral samples emitted just four times the number of alpha particles released by uranium. It was concluded that (1) uranium emits two alpha particles per disintegration, or (2) uranium consists of two distinct substances in equilibrium. The first possibility was eliminated by experiments of MARSDEN and BARRATT who showed that the alpha particles of uranium did not occur as doubles. Range measurements did show the existence of two distinct alpha groups of range 2.5 cm and 2.9 cm of air. Using the Geiger-Nuttall relationship a half-life of approximately $10^6$ years was calculated for this second component of uranium. (The presently accepted value of the half-life of $^{234}U$ is $2.5 \times 10^5$ years.) Attempts to separate the two radioactive components of uranium chemically were unsuccessful. Following these discoveries the early part of the uranium decay chain was written (incorrectly) in this way for some period of time: Uranium I $\rightarrow$ Uranium II $\rightarrow$ Uranium X $\rightarrow$ Ionium. We shall mention a little further on how this error came to be corrected.

Discovery of Radiothorium. Radiothorium was discovered by HAHN in 1905 shortly after he had joined Sir William Ramsay as a laboratory assistant. RAMSAY had given HAHN a sample of barium containing alpha activity believed to be radium and asked him to purify the radium according to the methods of Mme. CURIE and of GIESEL. This "radium" sample had been isolated not from an ordinary uranium ore but from thorianite, containing a high percentage of thorium, obtained from Ceylon. HAHN soon found that this preparation did not behave as did normal radium and in his experiments succeeded in isolating a new and very active substance which he called radiothorium. This substance gave rise to thorium X and thorium emanation. This made it necessary to revise previous views of the relationship of thorium X to thorium, as it had been thought that thorium X was the direct descendant of thorium.

Radiothorium is an isotope of thorium and it is clear in the light of later knowledge that its presence in Hahn's radium sample is to be explained.
by the isolation of mesothorium, an isotope of radium, with the barium carrier and by the subsequent growth of radiothorium into the sample.

**Discovery of mesothorium.** The discovery of mesothorium, the radium isotope which is the direct descendant of thorium, was the result of a slight controversy between HAHN and BOLTWOOD. HAHN had determined a value of about two years for the half-life of his newly-discovered radiothorium. BOLTWOOD had estimated a considerably longer half-life by an indirect method. BOLTWOOD had found that the activity of thorium oxide samples prepared from commercial samples was in some cases only about half the activity of thorium in minerals. This difference was attributed to the removal of radiothorium during chemical purification. If this were true, the rate of growth of activity back into the thorium should give the half-life of radiothorium, since radiothorium was then believed to be the direct descendant of thorium. The growth of activity, however, indicated a half-life of about six years, much longer than HAHN'S value.

HAHN deduced that the difference could be resolved if an unknown product intervened between thorium and radiothorium. To test this hypothesis HAHN obtained a series of thorium samples, whose dates of purification were known, from the firm of Knöfler and Company. HAHN found (1907) that the activity of thorium preparations was normal immediately after separation but gradually decreased with age to a minimum at about 4.6 years. After this, however, the activity then rose slowly toward the initial normal value. (This variation in thorium activity is shown exactly in Fig. 6.21) Using his previously determined value of two years for the half-life of radiothorium, HAHN deduced from the activity measurements that the intermediate substance did not emit alpha rays and was converted to radiothorium with a half-life of about 5.5 years. This new substance was called mesothorium.

\[
\text{Thorium} \xrightarrow{\text{5.5 yrs.}} \text{Mesothorium} \xrightarrow{\alpha} \text{Radiothorium} \xrightarrow{\text{2 yrs.}}
\]

BOLTWOOD later found that mesothorium was easily removed from thorium by precipitation of the thorium with ammonia. The original radiothorium remained with the thorium but new radiothorium at once commenced to grow into the mesothorium fraction. BOLTWOOD, SODDY, and MARCKWALD in separate investigations found that mesothorium was identical in chemical properties with radium.
Mesothorium 2. About one year after the discovery of mesothorium, HAHN reported that an activity with a half-life of 6.2 hours rapidly grew into freshly isolated samples of mesothorium. The 6.2 hour activity could be removed from mesothorium by precipitating a little zirconium or thorium with ammonia. The radiations from this new activity were interesting because of a prominence of several groups of monoenergetic electrons in contrast to the continuous spectrum of electron energies seen in the case of most beta emitters. This new activity was named mesothorium 2 and mesothorium itself was relabeled mesothorium 1.

Mesothorium was isolated in considerable quantity for commercial sale as a radium substitute. The 5.5 year half-life of mesothorium 1 (now known to be 6.7 years) was short enough to provide high specific activity material but still long enough to give a convenient working life for the samples. The mesothorium 2 which quickly grew into equilibrium and was maintained by the longer-lived parent emitted strong beta and gamma radiations which could be used for medical or other purposes. These commercial sources of mesothorium or "German radium" were usually not pure because the monazite sands from which they were prepared contained some uranium as well as thorium. Hence radium was isolated with the mesothorium.

Actinium X and Radioactinium. Independent work by GODLEWSKI and GIESEL (1905) showed that if actinium is precipitated with ammonia a new substance called actinium X remains in the solution. GODLEWSKI determined a half-life of 10.2 days for this substance. It was found to be a parent of the actinium emanation. Actinium X has properties similar to thorium X and to radium. HAHN (1906) found that the actinium X was not produced directly from the decay of actinium but that an intermediate alpha ray product, radioactinium, came between actinium and actinium X. The half-life of radioactinium was found to be 19.5 days.

When the series of radioactive changes in the active deposit of the actinium emanation was worked out the decay chain for actinium could be written (1912) as follows:

\[
\begin{align*}
\text{Actinium} & \xrightarrow{\beta} \text{Radioactinium} \xrightarrow{\alpha} \text{Actinium X} \xrightarrow{\alpha} \text{Actinon} \xrightarrow{\alpha} \\
\text{Actinium A} & \xrightarrow{\alpha} \text{Actinium B} \xrightarrow{\beta} \text{Actinium C} \xrightarrow{\alpha} \text{Actinium D}.
\end{align*}
\]

Except for some later information on the actinium C branch products and a small alpha branching of actinium itself this sequence is complete and
correct. However, at this time there was great uncertainty as to the origin of actinium itself.

Discovery of Uranium Y. The first crude estimate of the half-life of actinium reported by Mme. Curie in 1911 gave a value of about 30 years and a later measurement by Hahn and Meitner gave about 20 years indicating that some other radioactive product in pitchblende must be continuously replenishing the actinium. The search for this parent was unavailing for many years. It was not possible to separate actinium completely enough from the rare earths with which it was always mixed so that an atomic weight determination could be made. Nor could this be done for any disintegration product of actinium. The one fact that seemed to provide a clue was that the actinium content of any uranium mineral always bore a constant small ratio, in terms of disintegrations per unit time, to the amount of uranium. This led to the belief that actinium stood in some genetic relationship to the uranium decay chain and that it might arise from a small branching of uranium or one of its main-line decay products. In 1911 Antonoff reported his results on a new product, designated uranium Y, which could be isolated together with uranium X from uranium solutions by precipitation of ferric hydroxide. The amount of the 1.5-day uranium Y was small compared to uranium X. It did not appear to be genetically related to uranium X and its presence was most logically explained as being due to a branching decay of uranium, most probably at uranium 2. The possibility that uranium Y was related to actinium and might even be its immediate parent was considered. It became clear that uranium Y could not be the immediate parent of actinium for otherwise actinium would be observed to grow into pure uranium at a detectable rate.

Discovery of Protactinium and the Origin of Actinium. Some years later a new search was made for the parent of actinium using the Soddy-Fajans displacement rules of alpha and beta decay which we shall discuss presently. From its chemical properties actinium clearly belongs in Group III of the periodic chart. If the parent of actinium were an alpha emitter it should be placed in Group V in the eka-tantalum position. This parent must be long-lived to explain the past difficulties in observing the growth of actinium into purified uranium. Following these considerations Hahn and Meitner searched for a long-lived alpha emitter with chemical properties of eka-tantalum in the suitable residues from pitchblende processing. They succeeded (1918)
in isolating a new alpha emitting activity and demonstrated the growth of actinium into their samples. At this time they were unable to isolate a quantity in sufficient purity to determine the specific activity; however, they were able to estimate a half-life in the range 1200 to 180,000 years using the GEIGER-NUTTALL relationship. The new isotope was named protactinium. This was not the first isotope of the element to be discovered for FAJANS and GÖHRING had previously identified the isotope, UX₂.

At about the same time as the work of HAHN and MEITNER independent work by SODDY and CRANSTON had also shown the existence of protactinium which they called ekatantalum. Their chemical separation technique was based on the known volatility of tantalum chloride at high temperatures. They heated pitchblende in a stream of carbon tetrachloride and found that the material which sublimed out gave rise to actinium.

The discovery of protactinium made it possible to write the early part of the actinium chain as follows:

\[
\text{Uranium II} \xrightarrow{\text{branch}} \text{Uranium Y} \xrightarrow{\beta} \text{Protactinium} \xrightarrow{\alpha} \text{Actinium.}
\]

The correct assignment of the origin of uranium Y and a final settlement of the relationship of the actinium series to the other three series were not made for many years, but were finally achieved by the following developments.

(1) In 1929 ASTON found a small amount of Pb²⁰⁷ by examining the isotopic composition of lead obtained from a uranium mineral. From the high ratio of Pb²⁰⁷ to Pb²⁰⁸ in the sample it was clear that Pb²⁰⁷ could not be present simply because of contamination with ordinary lead. RUTHERFORD concluded from ASTON'S experiment that Pb²⁰⁷ must be in part due to actinium-lead, the end product of the actinium series. Assuming this to be correct, one could conclude that the atomic weight of protactinium must be 231 since six alpha particles are emitted in converting protactinium into actinium lead. This in turn meant that the uranium isotope from which protactinium is derived cannot be uranium II but must be an unknown isotope of mass 235, termed actinouranium. A. PICARD had hypothesized the isotope U²³⁵ as early as 1917.

(2) Definite evidence for a uranium isotope of mass 235 was obtained by the mass-spectrographic analysis of DEMPSTER in 1935. The first accurate
measurement on the isotopic composition of uranium was reported by NIER in 1939. NIER reported a value of 0.72\% for $^{235}\text{U}$ and also for the first time observed uranium $^{234}$, the uranium II of the uranium-radium decay chain.

(3) The atomic weight of protactinium was determined by A.V. GROSSE in 1935 by preparing, weighing, and analyzing a pure compound of the element. He reported a value of 230.6 ± 0.5.

The Concept of Isotopes and the Displacement Laws. During the first decade and a half of radioactivity when a large number of radioelements were being discovered two important perplexing facts were forced on the attention of most of the principal investigators in the field. The first was that the number of radioelements was much larger than the number of places available in the periodic chart on any reasonable extension of the periodic system of the element as it was then known. The number of different radioelements was in the neighborhood of thirty and these somehow had to be fitted into the chart in the elements between lead and uranium. Secondly, a number of the radioelements showed a truly remarkable chemical similarity to each other or to one of the previously known inactive elements. For example, it had been found impossible to separate ionium from thorium, radiolead from ordinary lead, mesothorium-1 from radium, uranium II from uranium I, etc. These perplexities were removed in 1913 by the introduction of the concept of the isotope and of the so-called displacement laws. The clearest statement of the new concepts was made by SODDY and independently by FAJANS although many persons such as FLECK and RUSSELL shared in this important discovery. The term "isotope" or "isotopic element" was suggested by SODDY for a group of two or more elements of different atomic weight occupying the same place in the periodic table and being in consequence chemically non-separable and identical. Under this concept radiolead and ordinary lead are not elements with remarkable chemical similarity but merely different forms of the same element. The element thorium thus had at least six different forms of differing atomic weight, these being thorium, ionium, radioactinium, radiothorium, uranium Y, and uranium X. The displacement laws were formulated by SODDY as follows:

1. The product resulting from an alpha transition is shifted two places in the periodic chart in the direction of diminishing mass from the place of the original substance.
2. The product resulting from a beta transition is shifted one place in the direction of the higher elements from that of the original substance.

These rules and the isotope concept assisted enormously in the placement of the radioactive products of the three series and in making understandable the chemical behavior of the elements. Shortly after the formulation of the displacement laws the Moseley concept of atomic number became a cornerstone of nuclear science and made even more explicit the meaning of the transformation laws. These new concepts assisted the search for new products and the correction of errors. An interesting example of this is the placement of uranium II in the early part of the uranium decay chain. We have reported previously how from radioactivity evidence the chain had been written:

\[
\text{Uranium I } \xrightarrow{\alpha} \text{Uranium II } \xrightarrow{\alpha} \text{Uranium X } \xrightarrow{\beta} \text{Ionium } \xrightarrow{\alpha} \text{Radium}
\]

Application of the displacement laws immediately showed that this could not be correct because uranium II should then be an isotope of thorium and easily separable from uranium I (mass number 238). Uranium II was in fact inseparable from uranium I. Hence the chain was rewritten as follows:

\[
\text{Uranium I } \rightarrow \text{Uranium X } \rightarrow \text{Uranium II } \rightarrow \text{Ionium } \rightarrow \text{Radium}
\]

This scheme still had one serious flaw. In view of the displacement laws, uranium X, an isotope of thorium, could not be expected to transform itself in a single beta transition to uranium II, an isotope of uranium. To correct this, RUSSELL and FAJANS presented the hypothesis that an unknown beta emitter must exist between uranium X and uranium II and that this substance should have properties similar to tantalum. FAJANS and GöHRING (1913) used tantalum as a carrier to isolate a new radioactive element with a half-life of 1.15 minutes. This activity was given the name UX₂. This was the first isotope to be discovered of the element which we now call protactinium. At the time of their discovery of UX₂ FAJANS and GöHRING suggested the name brevium because of the short half-life. Later when the isotope protactinium was found by HAHN and MEITNER the name brevium was abandoned, with Fajan's consent, in favor of protactinium as the name of the new element.

**Discovery of UX₂ - The First Isomer.** We shall close this account of the early years of radioactivity with a mention of one radioactive isotope whose chief importance lies in the fact that it was the first instance of isomerism to be discovered. As we have previously mentioned FAJANS and
GOHRING found that $UX_2$, a 1.15-minute isotope of element 91, was produced by the disintegration of $UX$, a 24.1 day isotope of thorium. Somewhat later (1921) HAHN showed that $UX_1$ gave rise not only to $UX_2$ but in a very small proportion of its disintegrations to a new substance named uranium Z. Uranium Z has a half-life of 6.7 hours and emits beta rays. From its origin and from its chemical properties it had to be regarded as an isotope of protactinium and what was more significant as an isotope identical in mass number with $UX_2$. This was the first instance of a phenomenon later to be termed "isomerism". (STEFAN MEYER had already indicated the possibility of the existence of such nuclear species which he had termed "isotopes of higher order".) It was not until the occurrence of nuclear isomers among artificially-radioactive isotopes was shown to be a general phenomenon that the nature of $UZ$ was completely understood.

Conclusion. This account of the early period of radioactivity brings us approximately to the year 1920 at which time the majority of products of the naturally-occurring radioactive series had been identified. Some more branch products were discovered later and, as we have mentioned, the important isotope $^{235}U$ was found in the late nineteen thirties. The main emphasis of the next decade before the discovery of artificial radioactivity was placed on a detailed study of the radiations of the individual isotopes. Hence at this point we shall conclude this review of the early period and turn to a systematic review of the properties of the naturally-occurring isotopes.

The reader who is interested in more detailed information on the early history of radioactivity can turn to the publications given below.
REFERENCES ON EARLY HISTORY OF NATURAL RADIOACTIVITY

"Natural Radioactivity", Encyclopaedia Brittanica.


"Oeuvres de Marie Sklogoowska Curie", collected by Irene Joliot Curie, Polish Academy of Sciences, Warsaw 1954.


6.2 THE URANIUM - RADIUM SERIES  
(THF 4n + 2 SERIES)

We now proceed to a more systematic discussion of the naturally-occurring radioactivities starting first with the uranium-radium series. Figure 6.2 shows this decay chain and Table 6.1 lists essential data for each isotope. The modes of decay are listed for each isotope but the radiations are not given in detail at this point. Each isotope is listed according to the standard isotopic designation and also according to the classical generic names. Although these classical symbols were chosen, as we have seen, before the isotopic identities were known, the older nomenclature still retains some attractive features. For example, all of the A-products are the immediate alpha-decay descendents of the noble gas isotopes in the three series so that radium A(RaA) immediately suggests the polonium daughter of the emanation whereas the symbol Po\(^{218}\) may require some reflection to associate it with radium preparations. Similarly the B-products in all three series are lead isotopes which decay to the C-products which are all bismuth isotopes. The C-products in turn undergo branched decay to the C'-products (polonium isotopes) and the C'' products (thallium isotopes).

A point of nomenclature which demands clarification is the family name for the isotopes of element 86, the noble gas. This element is perhaps most often termed radon which is also the isotopic designation for radium emanation. However, we prefer to adopt the family name emanation (Symbol Em) which has also been used. (See for example K. Fajans, Radioaktivität und die Neueste Entwicklung der Lehre von den Chemischen Elementen, F. Vieweg et Sohn, Braunschweig, 1919, p.94.

We shall also frequently refer to the uranium-radium series as the 4n + 2 series, the thorium series as the 4n series, etc., in recognition of the fact that the mass number of all members of a single series are divisible by four with a common remainder. This results from the fact that alpha decay always causes a change of 4 in mass number while beta decay proceeds without any change in mass number.

The Uranium Isotopes in Natural Uranium. Natural uranium consists of three alpha-emitting isotopes: \(^{238}\)U (Uranium I) present in 99.27 percent abundance, \(^{234}\)U (Uranium II), and \(^{235}\)U (actinouranium). \(^{238}\)U is the primary
Fig. 6.2. The uranium-radium series.
Table 6.1. The Uranium-Radium Series

<table>
<thead>
<tr>
<th>Radioelement</th>
<th>Symbol</th>
<th>Radiation</th>
<th>Half-life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium I</td>
<td>$U^{238}$</td>
<td>$\alpha$</td>
<td>$4.507 \times 10^9$ y</td>
</tr>
<tr>
<td>Uranium X₁</td>
<td>$Th^{234}$</td>
<td>$\beta$</td>
<td>24.1 d</td>
</tr>
<tr>
<td>Uranium X₂</td>
<td>$Pa^{234}$</td>
<td>$\beta$</td>
<td>1.175 m</td>
</tr>
<tr>
<td>Uranium Z</td>
<td>$Pa^{234}$</td>
<td>$\beta$</td>
<td>6.7 h</td>
</tr>
<tr>
<td>Uranium II</td>
<td>$U^{234}$</td>
<td>$\alpha$</td>
<td>$2.48 \times 10^5$ y</td>
</tr>
<tr>
<td>Ionium</td>
<td>$Th^{230}$</td>
<td>$\alpha$</td>
<td>$7.52 \times 10^4$ y</td>
</tr>
<tr>
<td>Radium</td>
<td>$Ra^{226}$</td>
<td>$\alpha$</td>
<td>1622 y</td>
</tr>
<tr>
<td>Radon</td>
<td>$Em^{222}$</td>
<td>$\alpha$</td>
<td>3.825 d</td>
</tr>
<tr>
<td>Radium A</td>
<td>$Po^{218}$</td>
<td>$\alpha$ and $\beta$</td>
<td>3.05 m</td>
</tr>
<tr>
<td>Radium B</td>
<td>$Pb^{214}$</td>
<td>$\beta$</td>
<td>26.8 m</td>
</tr>
<tr>
<td>Astatine 218</td>
<td>$At^{218}$</td>
<td>$\alpha$</td>
<td>2 s</td>
</tr>
<tr>
<td>Radium C</td>
<td>$Bi^{214}$</td>
<td>$\beta$ and $\alpha$</td>
<td>19.7 m</td>
</tr>
<tr>
<td>Radium C'</td>
<td>$Po^{214}$</td>
<td>$\alpha$</td>
<td>$1.58 \times 10^{-4}$ s</td>
</tr>
<tr>
<td>Radium C''</td>
<td>$Tl^{210}$</td>
<td>$\beta$</td>
<td>1.32 m</td>
</tr>
<tr>
<td>Radium D</td>
<td>$Pb^{210}$</td>
<td>$\beta$</td>
<td>19.4 y</td>
</tr>
<tr>
<td>Radium E</td>
<td>$Bi^{210}$</td>
<td>$\beta$ and $\alpha$</td>
<td>5.02 d</td>
</tr>
<tr>
<td>Radium F</td>
<td>$Hg^{206}$</td>
<td>$\beta$</td>
<td>8.6 m</td>
</tr>
<tr>
<td>Thallium 206</td>
<td>$Po^{210}$</td>
<td>$\alpha$</td>
<td>138.4 d</td>
</tr>
<tr>
<td>Radium G</td>
<td>$Tl^{206}$</td>
<td>$\beta$</td>
<td>4.19 m</td>
</tr>
<tr>
<td>Radium H</td>
<td>$Pb^{206}$</td>
<td>stable</td>
<td></td>
</tr>
</tbody>
</table>

Half-lives are given in years (y), days (d), and microyears (μy).
source material from which all the other (secondary) members of the uranium-radium series are derived since only $^{238}\text{U}$ is sufficiently long-lived to have existed since the formation of the elements. A small amount of $^{234}\text{U}$ must be found in every uranium sample in which radioactive equilibrium has been established. The ratio of atoms of $^{234}\text{U}$ to $^{238}\text{U}$ is simply the ratio of the half-lives or $5.5 \times 10^{-5}$. The equilibrium under discussion is given by the chain:

$$
\begin{align*}
\text{UI} & \xrightarrow{\alpha} \text{UX}_1 \xrightarrow{\beta^-} \text{UX}_2 \xrightarrow{\beta^-} \text{UII} \xrightarrow{\alpha} \\
& \quad \text{4.5} \times 10^9 \text{ yr.} \quad \text{24.1 day} \quad \text{1.17 min.} \quad \text{2.5} \times 10^5 \text{ yr.}
\end{align*}
$$

The $^{235}\text{U}$ present in natural uranium is unrelated to the $4n + 2$ series and in the long-lived primary isotope from which all secondary members of the actino-uranium series are derived.

The isotopic composition of natural uranium and the half-lives of the uranium isotopes are of quite fundamental importance for such diverse matters as the derivation of radioactive constants for other members of the decay chain, the preparation of counting standards, the age of minerals and the heat balance of the earth. Hence, we shall summarize the best values for these quantities.

DEMPSTER$^1$ first detected $^{235}\text{U}$ in natural uranium and reported an isotopic abundance of less than one percent. The first accurate mass-spectrographic analyses were made by NIER$^2$ who also detected $^{234}\text{U}$ for the first time.

The results obtained in NIER'S work and in several more recent studies are given in Table 6.2. Among the best recent work on the abundance of $^{238}\text{U}$ and $^{235}\text{U}$ is that of LOUNSBURY.$^3$ The half-lives of $^{238}\text{U}$ and $^{234}\text{U}$ have been calculated from the mass spectrographic results and from specific activity measurements on samples of natural uranium. These calculations require a

knowledge of the half-life of $^{235}\text{U}$ which has to be determined by some independent method. However, the contribution of $^{235}\text{U}$ to the total alpha activity of normal uranium is less than 5 percent, so large errors in the $^{235}\text{U}$ half-life are not reflected in similar errors in the calculation of the half-lives of $^{234}\text{U}$ and $^{238}\text{U}$.

Since the introduction of large-scale plants for the gaseous diffusion and electromagnetic separation of uranium isotopes it has been possible to make direct determinations of the half-lives of the uranium isotopes by specific activity measurements on samples highly enriched in $^{234}\text{U}$ and $^{235}\text{U}$. FLEMMING, GHIORSO and CUNNINGHAM have measured the half-lives of $^{234}\text{U}$ and $^{235}\text{U}$ on such enriched samples and have given a detailed and critical evaluation of the errors involved in such determinations. Table 6.2 contains a summary of the principal half-life determinations. We adopt the "best" values selected by FLEMMING. The table also lists various determinations of the isotopic composition of natural uranium. In Part III of Table 6.2 we quote "best" values for the isotopic composition. To construct this table we accepted LOUNSbury's $^{238}\text{U}/^{235}\text{U}$ atomic ratio of $137.8 \pm 0.14$ and FLEMMING'S "best" values for the half-lives of the isotopes and for the specific activity of natural uranium.

---

Table 6.2 Values of Radioactivity Constants for the Uranium Isotopes Occurring in Nature

PART I

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-life (years)</th>
<th>Specific Activity (disint/min. mg)</th>
<th>Decay Constant $\lambda$ in yrs$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{234}\text{U}$</td>
<td>$(2.7 \pm 0.27) \times 10^5$</td>
<td>$(1.3 \pm 0.13) \times 10^7$</td>
<td>$2.79 \times 10^{-6}$yr$^{-1}$</td>
<td>&quot;Best Value&quot;</td>
</tr>
<tr>
<td></td>
<td>$(2.29 \pm 0.14) \times 10^5$</td>
<td>$(1.48 \pm 0.09) \times 10^7$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(2.35 \pm 0.14) \times 10^5$</td>
<td>$(1.44 \pm 0.09) \times 10^7$</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(2.522 \pm 0.008) \times 10^5$</td>
<td>$(1.345 \pm 0.004) \times 10^7$</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(2.67 \pm 0.04) \times 10^5$</td>
<td>$(1.27 \pm 0.02) \times 10^7$</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(2.475 \pm 0.016) \times 10^5$</td>
<td>$(1.370 \pm 0.009) \times 10^7$</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(2.48 \pm 0.02) \times 10^5$</td>
<td>$(1.37 \pm 0.01) \times 10^7$</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>$^{235}\text{U}$</td>
<td>$(7.06 \pm 0.21) \times 10^8$</td>
<td>$(4.78 \pm 0.14) \times 10^3$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(8.8 \pm 1.1) \times 10^8$</td>
<td>$(3.82 \pm 0.49) \times 10^3$</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(7.13 \pm 0.16) \times 10^8$</td>
<td>$(4.74 \pm 0.10) \times 10^3$</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$8.91 \times 10^8$</td>
<td></td>
<td>6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(7.53 \pm 0.23) \times 10^8$</td>
<td>$(4.48 \pm 0.14) \times 10^3$</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(7.13 \pm 0.14) \times 10^8$</td>
<td>$(4.74 \pm 0.09) \times 10^3$</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>$^{238}\text{U}$</td>
<td>$(4.49 \pm 0.01) \times 10^9$</td>
<td>$742.7 \pm 1.6$</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(4.51 \pm 0.01) \times 10^9$</td>
<td>$738.6 \pm 1.6$</td>
<td>&quot;Best Value&quot;</td>
<td></td>
</tr>
</tbody>
</table>

1501 ± 6
1501 ± 3
1502 ± 1.5
1501 ± 3

"Best Value"
PART II
Composition of Natural Uranium (Literature Values)

<table>
<thead>
<tr>
<th>Atom Ratio $U^{238}/U^{235}$</th>
<th>Abundance $U^{234}$</th>
<th>Atom %</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$138.9 \pm 1.4$</td>
<td>0.0059 ± 0.00059</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$137.0 \pm 0.7$</td>
<td>0.00555 ± 0.00017</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>$138.0 \pm 0.3$</td>
<td>----</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>$139$</td>
<td>0.00504 ± 0.00030</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>$137.8$</td>
<td>----</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>$137.8 \pm 0.14$</td>
<td>----</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.00557 ± 0.00006</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>$138.0 \pm 1.4$</td>
<td>0.00545 ± 0.00004</td>
<td>14</td>
<td></td>
</tr>
</tbody>
</table>

PART III
"Best Values" Composition of Natural Uranium

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Abundance (Atom percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$234$</td>
<td>0.0055 ± 0.0002</td>
</tr>
<tr>
<td>$235$</td>
<td>0.7204 ± 0.0007</td>
</tr>
<tr>
<td>$238$</td>
<td>99.2741 ± 0.0007</td>
</tr>
</tbody>
</table>

Atom Ratio $U^{238}/U^{234} = 18.180 ± 550$
Atom Ratio $U^{238}/U^{235} = 137.80 ± 0.14$
Specific Activity = 1501 ± 3 dis/min mg total uranium
Contribution of $U^{235} = 33.7 ± 0.7$
Contribution of $U^{238} = 733.6 ± 1.6$
Contribution of $U^{234} = 733.6 ± 1.6$
References to Table 6.2

1. A.O. Nier, Phys. Rev. 55, 150, 153 (1939); $^{235}\text{U}$ half-life recalculated in accordance with the work of KOVARIK and ADAMS.


10. "Best values" taken from Fleming et al. Ref. 5.


14. Calculated as described by Fleming et al., Ref. 5 using "best values" of specific activities of $^{235}\text{U}$, $^{234}\text{U}$ and natural uranium and the $^{238}\text{U}/^{235}\text{U}$ atom ratio. These values constitute a self-consistent set.
One milligram of pure natural uranium emits exactly 1501 alpha particles per minute. Of these 733.6 are emitted by $^{238}\text{U}$, an equal number by $^{234}\text{U}$ and 33.7 are emitted by $^{235}\text{U}$. Pure uranium grows daughter alpha-activity only at a very slow rate because of the long half-life of ionium; it would take several hundred years before the alpha activity of pure natural uranium increased by one percent. The growth curve for ionium appears in Fig. 6.4. The energy of the main group of alpha particles of $^{238}\text{U}$ and $^{235}\text{U}$ have been measured as $4.195 \pm 0.005$ MeV and $4.768 \pm 0.003$ MeV, respectively, by the gridded ion-chamber technique. In addition, each isotope has a group of alpha particles in about 25 percent abundance approximately 50 keV smaller in energy and a third group approximately 160 keV lower in energy in a few tenths of one percent abundance. The alpha spectrum of $^{235}\text{U}$ is complex as described in Chapter 8 (See section 8.4.9).

Pure uranium emits no beta particles and essentially the only gamma radiation associated with $^{238}\text{U}$ and $^{234}\text{U}$ is 45 keV and 52 keV $\gamma$-radiation, respectively, which is very low in abundance. These transitions have been studied chiefly through their conversion electrons. The growth of $\text{UX}_1$ and $\text{UX}_2$ soon introduces hard beta and gamma radiation into uranium. This beta activity reaches equilibrium in undisturbed samples several months after the last purification of the uranium as shown in Fig. 6.3.

Uranium $\text{X}_1$ ($\text{Th}^{234}$) and Uranium $\text{X}_2$ ($\text{Pa}^{234}$). The growth of $\text{UX}_1$ into pure uranium is shown in Fig. 6.3. Because $\text{UX}_2$ has a half life of only 1.17 minutes it comes to equilibrium with $\text{UX}_1$ within a few minutes. Hence, Fig. 6.3

6. G.E. Kocharov, A.P. Komar and G.A. Korolev, Zhur. Eksptl. i. Teoret. Fiz. 36, 68 (1959) report abundances of 23 ± 4 percent and 23 ± 0.07 percent for alpha groups leading to levels in the $\text{Th}^{234}$ daughter of 48 ± 4 keV and 160 ± 5 keV, respectively.
8. The Photons and Conversion Electrons of the 52 keV Transition in $^{234}\text{U}$ Decay were studied by the following authors: G. Scharff Goldhaber in Report BNL-103, June 1951; P.R. Bell and co-workers in ORNL-1164, April 1952; A.A. Vorob'ev et al., Sov. Phys. JETP, 5, 516 (1957); and Teillac, Compt. Rend. 230, 1056 (1950).
Fig. 6.3. Growth of U(X_{\text{Th}^{234}}) into pure uranium (t_{1/2} of U(X_{\text{Th}} = 24.1 days).
can also be used to evaluate the growth of UX\textsubscript{2} into pure uranium. When equilibrium is reached the number of disintegrations per minute of U\textsuperscript{238} is precisely equal to the number of disintegrations per minute of UX\textsubscript{1} and UX\textsubscript{2}. Because of this equilibrium uranium is often employed as a standard of radioactive intensity for calibrating the counting efficiency of radiation detection equipment. A sample of pure uranium is analyzed by igniting a suitable compound to the oxide, U\textsubscript{3}O\textsubscript{8}, and weighing the oxide, or by some other standard analytical method. The disintegration rate is calculated, using the value 733.6 disintegrations per minute per milligram of normal uranium. The sample is usually covered with a foil of sufficient thickness (about 30 mg/cm\textsuperscript{2} aluminum) to filter out the soft beta particles of UX (end point energy = 193 keV) so that only the energetic beta rays of UX\textsubscript{2} are counted (end point energy = 2.32 MeV). This is done so that uncertain corrections due to absorption of soft electrons in the sample and in the counter window can be eliminated.

UX\textsubscript{1} is a convenient tracer for the element thorium. It can be readily isolated in carrier-free form from uranium using a number of chemical methods.

In the historical section we have shown how the discovery of the re-growth of UX \pm UX\textsubscript{2} beta activity into purified uranium and the decay of the 24.1 day UX activity, which had been separated from uranium by coprecipitation on barium sulfate, was of considerable importance in calling attention of early workers to the continuous production of radioactive matter from the decay of a parent element. UX\textsubscript{2} is of historical importance also because its discovery by PAJANS and GOHRING in 1913 constituted the first discovery of an isotope of element 91. They called the element brevium from the short half-life of UX\textsubscript{2} but when Pa\textsuperscript{231} was discovered in 1918 this name was dropped.

In the beta decay of Th\textsuperscript{234} the principal daughter product is the 1.17-minute UX\textsubscript{2}. However, in 0.14 percent of its disintegrations an isomeric form of Pa\textsuperscript{234}\textsuperscript{2} with a 6.66-hour half-life is produced. This activity has the special name of Uranium Z. It was discovered by HAHN in 1921 and constituted the first example of nuclear isomerism.

The UX\textsubscript{1} - UX\textsubscript{2} - UZ mixture emits a complex mixture of beta particles, gamma rays and conversion electrons. Present knowledge of these radiations and of the decay schemes of these nuclides is summarized in Chapter 8. (Sec. 8.2.12)
Ionium. Ionium was discovered by the American radiochemist BOLTWOOD in 1907. It is an isotope of thorium which decays by alpha emission with the relatively long half-life of $7.52 \times 10^4$ years. In Table 6.3 we note that 16 grams of ionium are to be found in an uranium ore sample containing one metric ton of uranium. Figure 6.4 shows the growth of ionium into pure uranium starting with an equilibrium mixture of Uranium I and Uranium II. The rate of growth is linear for many years and amounts to 0.147 micrograms per kilogram of uranium per year. The growth of radium into pure ionium is shown in Figure 6.5. The initial rate of growth, which is linear for many years, is 8.72 micrograms per year for one gram of ionium. This is $1.85 \times 10^{10}$ disintegrations per minute of Ra$^{226}$.

It is important to realize that ionium isolated from uranium ores is not isotopically pure, because of the presence of Th$^{232}$ in all uranium ores. The amount of thorium is quite variable and in the purest uranium ores may be quite low expressed as a ratio of thorium to uranium. However, the weight ratio of ionium to uranium is only 0.000017 so that a mere trace of thorium in the ore will cause a considerable isotopic dilution of the ionium isolated therefrom. ELIZABETH RONA$^{10}$ has studied the isotopic composition of thorium fractions isolated from a variety of uranium ores with the results shown in Table 6.4. From the standpoint of alpha activity the contribution of Th$^{232}$ to the specific activity of an ionium-thorium mixture containing an appreciable percentage of ionium is entirely negligible. The specific activity of one microgram of pure ionium is 45,700 disintegrations per minute whereas the specific activity of one microgram of pure Th$^{232}$ is only 0.246 disintegrations per minute.

Ionium is an excellent tracer for the radiochemical or the chemical behavior of thorium. Ionium and its daughter product, radium, are found in ocean sediments in amounts much greater than would be accounted for by the uranium content of the sediments. This is a consequence of the selective removal of ionium from sea water by ferric and manganic hydroxide. The


Fig. 6.4. Growth of ionium into chemically pure uranium consisting of the natural mixture of uranium isotopes. The ionium is expressed in units of mass and also in units of activity.
Table 6.3 Amount of Individual Nuclides Present in Unaltered Natural Uranium Ore Bodies Containing One Metric Ton of Uranium

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>U(^{238})</td>
<td>4.507 x (10^9) years</td>
<td>992.9 kilograms</td>
</tr>
<tr>
<td>U(^{235})</td>
<td>7.13 x (10^8) years</td>
<td>7.1 kilograms</td>
</tr>
<tr>
<td>U(^{234})</td>
<td>2.48 x (10^5) years</td>
<td>54 grams</td>
</tr>
<tr>
<td>Pa(^{231})</td>
<td>3.43 x (10^4) years</td>
<td>334 milligrams</td>
</tr>
<tr>
<td>Th(^{230}) (Ionium)</td>
<td>7.52 x (10^4) years</td>
<td>16 grams</td>
</tr>
<tr>
<td>Ac(^{227})</td>
<td>22.0 years</td>
<td>0.21 milligrams</td>
</tr>
<tr>
<td>Ra(^{226})</td>
<td>1622 years</td>
<td>340 milligrams</td>
</tr>
<tr>
<td>Pb(^{210}) (RaD)</td>
<td>19.4 years</td>
<td>3.77 milligrams</td>
</tr>
<tr>
<td>Po(^{210}) (RaF)</td>
<td>138.4 days</td>
<td>7.4 micrograms</td>
</tr>
</tbody>
</table>
Fig. 6.5. Growth of Ra\textsuperscript{226} into pure ionium.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral</th>
<th>Source</th>
<th>$\frac{\text{Th}^{232}}{\text{Th}^{230}}$</th>
<th>Uranium content (pct.)</th>
<th>$\frac{\text{Th}^{232}}{\text{U}^{238}} \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pitchblende</td>
<td>Joachimsthal, Czechoslovakia</td>
<td>0.00 ± 0.001</td>
<td>45.7</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Pitchblende</td>
<td>Cinch Lake, Uraninite Mine, Lake Athabaska, Sask. Canada</td>
<td>0.77 ± 0.01</td>
<td>----</td>
<td>14.1</td>
</tr>
<tr>
<td>3</td>
<td>Pitchblende</td>
<td>Eldorado Mines, Great Bear Lake N.W.T., Canada</td>
<td>1.55, 1.66</td>
<td>52.0</td>
<td>29.3</td>
</tr>
<tr>
<td>4</td>
<td>Pitchblende</td>
<td>Katanga</td>
<td>9.9, 9.50, 9.72</td>
<td>75</td>
<td>177.5</td>
</tr>
<tr>
<td>5</td>
<td>Pitchblende</td>
<td>Katanga</td>
<td>9.27, 9.40</td>
<td>75</td>
<td>170.7</td>
</tr>
<tr>
<td>6</td>
<td>Pitchblende</td>
<td>Katanga</td>
<td>7.0</td>
<td>75</td>
<td>139.0</td>
</tr>
<tr>
<td>7</td>
<td>Presumably Pitchblende</td>
<td>Unknown, Probably Great Bear Lake Region</td>
<td>2.86, 2.88</td>
<td>----</td>
<td>51.4</td>
</tr>
<tr>
<td>8</td>
<td>Pitchblende</td>
<td>Kirk Mine, Gilpin County, Colorado</td>
<td>27.9, 26.2</td>
<td>39.0</td>
<td>47.4</td>
</tr>
<tr>
<td>9</td>
<td>Uraninite</td>
<td>Wilberforce, Canada</td>
<td>53</td>
<td>60.0</td>
<td>969.4</td>
</tr>
<tr>
<td>10</td>
<td>Carnotite</td>
<td>Colo-Utah region</td>
<td>28.0</td>
<td>----</td>
<td>512.0</td>
</tr>
<tr>
<td>11</td>
<td>Samarskite</td>
<td>Mosambique, East Africa</td>
<td>1300</td>
<td>6.2</td>
<td>23,790</td>
</tr>
</tbody>
</table>
ionium and radium content of ocean sediments can be used to measure the age of sediments and to fix the dates of various geological eras. This subject is reviewed by RANKAMA and by PETTERSSON.

Ionium is a useful target material in many cyclotron bombardment studies, neutron irradiation studies, etc. For these purposes, the presence of Th contamination is troublesome as it results in the production of activities other than the ones it is desired to produce. For example, gram amounts of ionium, isolated by PEPPARD and his associates at the Argonne National Laboratory have been irradiated in high flux reactors in order to produce the valuable isotope Pa according to the following sequences of reactions.

\[
^\text{Io}^{230} (n,\gamma)^\text{Th}^{231} (UY) \rightarrow ^\beta^- \text{Pa}^{231}
\]

The capture cross section is 26 barns. This is a valuable procedure for the preparation of proctactinium because the isolation of protactinium in quantity from uranium ores has proved to be rather difficult. However, a difficulty with this artificial synthesis of Pa arises from the presence of Th in the ionium. The particular samples irradiated by PEPPARD contained 12% ionium and 88% Th by isotopic composition so that large amounts of the 27.4-day beta-emitter Pa were produced according to the sequence.

\[
^\text{Th}^{232} (n,\gamma)^\text{Th}^{233} \rightarrow ^\beta^- \text{Pa}^{233}
\]

\[\sigma = 7.55 \text{ barns}\]

The beta and gamma activity of this Pa is so huge that it necessitates the use of considerable shielding in the isolation of the protactinium.

---


Furthermore even when it is isolated the protactinium has an undesirable specific activity for beta and gamma radiation. Consequently, the protactinium must be stored for a few years to permit the decay of the Pa$^{233}$.

Difficulties of this type can be reduced by the use of isotopically enriched ionium. Some ionium has been separated at Oak Ridge by the electromagnetic process to produce ionium enriched to greater than 90% isotopic abundance. 14

Thorium ores usually contain some uranium and therefore purified thorium will contain ionium. The amount is always negligible in terms of weight percentage but, depending on the original uranium content of the ore, may not be negligible in terms of specific activity.

The alpha spectrum and the details of the decay scheme of ionium are discussed in Chapter 8. (See Section 8.2.8)

**Radium.** Radium was discovered by PIERRE CURIE, MARIE CURIE and G. BERMONT in 1898 at the Sorbonne in Paris. In 1902 Mme. CURIE prepared the first pure salt of radium after a tedious process of isolation in which several tons of pitchblende residues were treated. Radium is the heaviest member of the alkaline earth group of elements and has chemical properties similar to barium. Barium is frequently used as a carrier element in the isolation of radium. The name "radium" was originally applied only to the 1622 year radium occurring in the uranium decay series but later was adopted as the general name for element 86. Ra$^{226}$ is the longest-lived of all the radium isotopes and all studies of the physical and chemical properties of the element with weighable quantities of material are carried out with it.

Ra$^{226}$ is the immediate daughter of ionium in the uranium decay chain. The growth of radium into pure ionium is displayed in Fig. 6.5. The growth of radium into an equilibrium mixture of U$^{238}$ and U$^{234}$ containing no ionium or radium at zero time is shown in Fig. 6.6. Radium is present in natural minerals only because of its constant replenishment from ionium and from its ultimate parent, U$^{238}$, and hence is found primarily in uranium ores. Radium salts are quite soluble in water, however, and any uranium minerals subject

---

Fig. 6.6. Growth of radium into natural uranium after purification from ionium and radium. The uranium is assumed to consist initially of an equilibrium amount of U$^{238}$ and U$^{234}$. 

\[
\text{ACTIVITY RATIO } \frac{R^2_{26}}{U^{234}} = \frac{R^2_{26}}{U^{238}} = R^2_{26} / U^{238}
\]
to leaching may be deficient in radium content. Secondary minerals with a non-equilibrium excess amount of radium may form at a new site. Because of the leaching of radium from uranium ore bodies, small amounts of radium are found in springs, rivers and sea water. Ocean sediments contain non-equilibrium amounts of radium because of the adsorption of the ionium parent on basic materials on the ocean floor. References to the literature on such studies can be found in RANKAMA.\textsuperscript{11}

Radium and its daughter products played a prominent role in the early history of radioactivity as we have seen. For many years radium was of great commercial importance as a source of penetrating radiations for medical and radiographical purposes. For these applications it is the radiations of the daughter products which are chiefly effective since Ra\textsuperscript{226} itself emits only alpha particles and a 188-keV gamma ray. The immediate daughter of radium is radon (Rn\textsuperscript{222}) which has a half-life of 3.825 days and also emits only alpha particles. The next series of products RaA, RaB, RaC, RaC', and RaC'' are quite short-lived and rapidly come to transient equilibrium with the radon. A radium preparation in solid form from which the radon does not escape, or a sealed radium preparation, comes to equilibrium with these daughter products within a couple of weeks. The growth of radon into pure radium is shown in Fig. 6.7. The shape of the growth curve for RaA, RaB, RaC, RaC' and RaC'' growing into pure radium is nearly identical because their half-lives are short compared to that of radon.

The mixture of radium and its daughter products emits a very potent complex of gamma rays especially those contributed by RaC (Bi\textsuperscript{214}); see Table 6.12 below.

For medical purposes a radium compound (usually radium sulfate) is sealed in a platinum capsule which can be placed near the tissue to be irradiated. The walls of the capsule absorb the alpha rays completely but the penetrating gamma radiation is absorbed only slightly. Alternatively the radium source can be used simply as a source of radon which is periodically removed and compressed into a small glass capillary. This radon sample (plus products) is then used for application to the tissue. Radium is used primarily for treatment of cancer. In some applications (in particular, cancer of the cervix uteri) the use of radium therapy is routine and is successful in a high percentage of cases. In a good many other applications
Fig. 6.7. The growth of 3.825 day radon into pure radium.
the success of radium therapy is limited. The availability of radioactive isotopes from nuclear reactors or accelerators, or the use of high voltage x-ray machines, bevatrons, etc. has lessened the need for radium for medicinal purposes. This is also true for industrial radiography and other commercial application of radium.

Radium has been used widely in physical laboratories to prepare laboratory neutron sources. An intimate mixture of a radium salt and some light element such as beryllium will emit neutrons because of \((\alpha, n)\) reactions which occur in the mixture. This is discussed in Sec. 5.5.4 of Chapter 5.

**DECAY SCHEME OF RADIUM**

The alpha decay of radium is summarized in Fig. 6.8. Several measurements have been made of the energy of the main group in magnetic spectrometers.\(^15\)\textsuperscript{-17} For several years the best value was 4.777 MeV but a more recent and careful determination\(^18\) resulted in the value 4.782. This shift in energy was caused chiefly by a shift in the accepted value of the alpha energy of the alpha particles of Po\(^{214}\), which was used as an energy standard. A second alpha group in 6 percent intensity was reported from two laboratories.\(^19\),\(^20\) This group

\begin{itemize}
\item \textsuperscript{15} G. Bastin-Scoffier, Compt. rend. 233, 945 (1951).
\item \textsuperscript{16} G. Bastin-Scoffier and J. Santana-Dionisio, Compt. rend. 236, 1016 (1953).
\item \textsuperscript{17} S. Rosenblum, M. Perey, M. Valadares, and M. Guillot, private communication (Oct. 1952) quoted by Hollander, Perlman and Seaborg, Rev. Mod. Physics 25, 469 (1953).
\item \textsuperscript{18} R.J. Walen and G. Bastin, Comptes rendus Du Congres International de Physique, Paris, p. 910, July 1958.
\item \textsuperscript{19} Rosenblum, Guillot, Bastin-Scoffier, Compt. rend. 229, 191 (1949); S. Rosenblum, Compt. rend. 195, 317 (1932).
\item \textsuperscript{20} F. Asaro and I. Perlman, Phys. Rev. 88, 129 (1952).
\end{itemize}
and two additional groups of much lower intensity were discovered by WALEN and BASTIN in some experiments which exploited new techniques for reducing background effects in alpha spectroscopy. The results of this study are quoted in the table and summarized in Fig. 6.8.

The most prominent gamma radiation is the 186 keV transition which de-excites the first excited state. HAHN and MEITNER reported this transition in 1924. CORK measured the conversion electrons. ROY and GOES characterized the radiation as E2 by measurement of the K-conversion coefficient and the subshell conversion ratios. These results were confirmed by JURIC and STANOJEVIć. The E2 assignment was strengthened by the α-γ coincidence experiments of MILTON and FRAZER.

Very careful experimental technique is required to detect other gamma transitions because of their low intensity. STEPHENS reported a 260 keV gamma ray with an intensity only 1/400 of the 187 keV gamma ray and found it to be in coincidence with the 187 keV gamma ray. HARBOTTLE, McKEOWN and SCHARFF-GOLDFHABER also reported these results. In order to study a gamma ray of this low intensity in Ra it is necessary to remove radon continuously from the sample under investigation in order to avoid interference from gamma-emitters further down the decay chain. STEPHENS further reports a very low intensity 420 keV gamma ray, in coincidence with the 187 keV transitions, and a gamma ray of ~610 keV. The intensity of the known gamma rays per disintegration of Ra is the following: 187 keV (0.057); 260 keV (7 x 10^-5); 420 keV (2 x 10^-6); 610 keV (2 x 10^-6). There is a strong possibility that the 610 keV gamma ray originates at the level labeled 599 keV in the figure; the discrepancy in energy may be ascribed to experimental error.

Fig. 6.8. Decay scheme of Ra\textsuperscript{226}. Alpha energies are relative to Po\textsuperscript{218} E\textsubscript{\alpha} = 6.002 MeV.
Table 6.5 Alpha Particles of Ra$^{226}$

<table>
<thead>
<tr>
<th>$\alpha$-Particle Energy (MeV)</th>
<th>$\Delta E_{\alpha}$ (keV)</th>
<th>Energy of Excited State (keV)</th>
<th>Intensity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.782</td>
<td>0</td>
<td>0</td>
<td>94.6</td>
</tr>
<tr>
<td>4.5994 ± .0005</td>
<td>182.6</td>
<td>186</td>
<td>5.4</td>
</tr>
<tr>
<td>4.340 ± .001</td>
<td>441.5</td>
<td>449</td>
<td>$(5.1 \pm 0.3) \times 10^{-3}$</td>
</tr>
<tr>
<td>4.194 ± .004</td>
<td>588</td>
<td>599*</td>
<td>$(5 \pm 4) \times 10^{-4}$</td>
</tr>
</tbody>
</table>

R.S. Walen and G. Bastin, Comptes rendus du Congres International de Physique, Paris, July, 1958. Energies were measured relative to Po$^{218} E_{\alpha} = 6.002$ MeV.

*F. Stephens reports a 610 keV gamma ray in $2 \times 10^{-4}$% intensity which probably de-excites this state. Hence the true state energy may lie between 599 and 610 keV.
The energy level system of $^{222}$Rn observed in the decay of $^{226}$Ra is of some theoretical interest. The two $2^+$ states are believed to be quantum states of collective excitation of a nucleus which is spherical in its ground state but soft toward harmonic oscillations around the favored spherical shape. This matter is discussed more fully in Sec. 3.2 of Chapter 3. The $1^-$ state at 610 (or 599) keV is also believed to be a state of collective excitation related to general occurrence of negative parity states in even-even nuclei of the heavy elements. This class of nuclear excitation is discussed in Sec. 3.5.3 of Chapter 3.

Measurements of the Half-life of Radium. The practical unit of radioactivity, known as the Curie, was originally based upon the specific activity of radium and was defined as the number of disintegrations per second occurring in a gram of radium exclusive of its decay products. Hence it was of considerable importance to determine a precise value for the specific activity of radium. This turned out to be a problem of considerable difficulty because of the complications of daughter activity. A variety of methods gave values clustering around $3.7 \times 10^{10}$ disintegrations per second per gram for the specific activity and 1600 years for the half-life. Table 6.6 summarizes the principal determinations which have been made. In 1931 an international committee of distinguished workers in the field of radioactivity\(^{28}\) reviewed the experimental determinations up to that time and chose 1590 years as the best value. KOHMAN, AMES and SEDLET\(^{29}\) devoted considerable attention to this problem in 1945 and reported the value $1622 \pm 13$ years which value will be adopted in this book. A Russian redetermination by a calorimetric method as reported in the year 1958 gave a value of $(3.71 \pm 0.02) \times 10^{10}$ disintegrations sec$^{-1}$ gram$^{-1}$ corresponding to a half-life of $1577 \pm 9$ years.\(^{30}\) MARTIN and TUCK\(^{31}\) in 1959 critically evaluated all published information on disinte-

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Table 6.6. Summary of Experimental Determinations of the Specific Alpha Activity of Radium up to the year 1949.

<table>
<thead>
<tr>
<th>Method</th>
<th>Experimenters and reference</th>
<th>Value(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate of Ra evolution by Ra</td>
<td>J. D. Dodd, Proc. Roy. Soc. London, A81:150 (1905)</td>
<td>2.35 (^c)</td>
</tr>
<tr>
<td>Rate of Ra evolution by Ra</td>
<td>J. D. Dodd, Proc. Roy. Soc. London, A84:406 (1910)</td>
<td>5.75 (^d)</td>
</tr>
<tr>
<td>Heat generation by Ra particles</td>
<td>R. S. Balilwood and H. Rutherford, Phil. Mag., (6) 2: 586 (1911)</td>
<td>3.27 (^e)</td>
</tr>
<tr>
<td>Rate of Ra evolution by Ra</td>
<td>J. D. Dodd, Proc. Roy. Soc. London, A81:850 (1905)</td>
<td>5.85 (^f)</td>
</tr>
<tr>
<td>Heat generation rate of Ra particles</td>
<td>F. P. Born, Wiss. Ber., (11a) 121: 142 (1932)</td>
<td>3.75 (^g)</td>
</tr>
<tr>
<td>Electrical charge of Ra particles from Ra and descendants</td>
<td>J. D. Dodd and V. Danse, Am. J. Sci., (4) 29: 810 (1915)</td>
<td>3.25 (^h)</td>
</tr>
<tr>
<td>Growth rate of Ra in to</td>
<td>E. Geiger, Am. J. Sci., (4) 11: 312 (1916)</td>
<td>3.33</td>
</tr>
<tr>
<td>Growth rate of Ra in to</td>
<td>B. M. W. Leven, Wiss. Ber., (11a) 127: 40 (1928)</td>
<td>3.75</td>
</tr>
<tr>
<td>Visual counting of galvanometer deflections from Ra C 0 particles in proportional counter</td>
<td>V. P. Born and H. W. Leven, Wiss. Ber., (11a) 127: 405 (1928)</td>
<td>3.75</td>
</tr>
<tr>
<td>Photographic oscillographic counting of Ra C 0 particles proportional counter</td>
<td>E. Geiger and A. Veres, S. Physik, 21: 187 (1911)</td>
<td>3.45</td>
</tr>
<tr>
<td>Visual counting of scintillations from Ra and descendants by the observers</td>
<td>L. Vernet, Ann. Phys., (7) 6: 17 (1908)</td>
<td>3.68 (^i)</td>
</tr>
<tr>
<td>Visual counting of scintillations from Ra and descendants by the observers</td>
<td>L. Vernet, Ann. Phys., (7) 6: 17 (1908)</td>
<td>3.68 (^j)</td>
</tr>
<tr>
<td>Electric charge of Ra particles from Ra (\alpha ) deposit</td>
<td>H. J. Jentschke, Compt. rend., 155: 291 (1912); Ann. Phys., (3) 9: 285 (1925)</td>
<td>3.50 (^k)</td>
</tr>
<tr>
<td>Comparison of ionization of single Ra C 0 particles with gross ionization from Ra C 0 deposit</td>
<td>E. J. Inggarf, S. Physik, 46: 608 (1920)</td>
<td>3.75</td>
</tr>
<tr>
<td>Rate of Ra evolution by Ra</td>
<td>T. F. Bens, E. F. W. Leven, Wiss. Ber., (11a) 121: 142 (1932)</td>
<td>3.75 (^s)</td>
</tr>
<tr>
<td>Electrical counting of Ra particles from Ra (\alpha ) deposit and purified Ra (\beta ) in ionization chamber</td>
<td>T. F. Bens, E. F. W. Leven, Wiss. Ber., (11a) 121: 142 (1932)</td>
<td>3.75 (^t)</td>
</tr>
</tbody>
</table>

This table prepared by Goodnow, Jones and Belfet, 1949

\(^a\) In units of 1 x 10\(^9\) particles per second per gram.


\(^c\) Calculated from and/or by following paper.

\(^d\) Corrected according to following paper.

\(^e\) Corrected from best generation rate given using currently accepted value of Ra disintegration energy.

\(^f\) Recalculated using currently accepted value of electronic charge.

\(^g\) Recalculated using currently accepted value of Avogadro number.

\(^h\) Recalculated using currently accepted value of electronic charge.

\(^i\) Recalculated using currently accepted value of Loschmidt number.

\(^j\) Recalculated using currently accepted value of Ra disintegration energy.

\(^k\) Corrected by authors elsewhere.
gration energies in the radium series and combined them with the calorimetric measurements of MANN\textsuperscript{32} for the heating effects of several national primary standards to derive a specific activity for radium of $3.655 \times 10^{10}$ disintegrations per second per gram corresponding to a half-life of 1602 years.

It can be seen from these values, even the most recent ones, that the disintegration rate of radium is still uncertain to a few percent. In recent years the attempt to identify the Curie unit of activity with the specific activity of radium was abandoned. The Curie has been redefined as $3.700 \times 10^{10}$ disintegrations per second. Nonetheless, it would be desirable and is within the reach of present techniques to reduce the uncertainty in the radium half-life to less than one percent.

Assay Methods for Radium. The accurate measurement of quantities of radium is important in experimental research, in radium therapy, and in commercial applications and can be done by several essentially different methods. These methods are outlined below. More detailed information can be found in the references listed in Table 6.7.

1. Radium Analysis by Measurement of Radium Alpha Particles. For small samples the disintegration rate can be determined by counting the alpha particles from the samples or from an accurately measured aliquot. The contribution of radon and other daughter products to the counting rate cannot be calculated because of the variable retention of radon in the sample, but can be determined by alpha spectrum analysis. In this method, a sample of radioactivity (thin compared to the range of the alpha particles) is placed in an ionization chamber of sufficient size that the alpha particles expend their entire range in the chamber, and the pulse developed from the charge collected on the positive electrode is subjected to pulse height analysis. From the pulse height spectrum and the known energies and abundances of the alpha particle groups from radium and its daughters the disintegration rate of the $^{226}$Ra in the sample can be determined. This method is accurate to a few percent. It is used chiefly for small samples in research studies. Solid

Table 6.7 Bibliography on Techniques for Estimation of Radium Content.

state counters may be substituted for the ionization chamber.

2. The Gamma-ray Method of Radium Analysis. A radium salt sealed in a tube so that no radon can escape will be in equilibrium after about one month (see Fig. 6.7) with radon and its short-lived descendents and will therefore emit energetic gamma-rays (particularly those from RaC) with an intensity proportional to the amount of radium present. The intensity of the gamma-radiation from the preparation to be tested is compared with that due to a standard sample containing a known quantity of radium. The gamma-radiation is measured with some sort of electroscope, ionization chamber or other radiation detector. The contribution from beta activity is removed by absorbers or by using sufficiently thick-walled detecting instruments. When properly used, this method is accurate to about one-half of a percent but the accuracy which is ordinarily achieved may be only 1.5 percent. The accuracy can be improved by using the detection instrument as a null instrument. For example, RUTHERFORD and CHADWICK\textsuperscript{33} devised a balance method in which the ionization current caused in a lead ionization chamber by the gamma radiation from a sample is balanced against an equal and opposite ionization current supplied by some constant source of radiation such as uranium oxide in another ionization chamber. The balance distances are determined for the unknown sample and for the standard radium sample with which it is to be compared. The accuracy of this method approaches a quarter of one percent.

The gamma-ray method has the advantage that the radium itself is undisturbed within its sealed tube. It is well suited for quantities ranging from 10 micrograms to one gram. It is not applicable to radium samples containing appreciable amounts (by activity) of mesothorium because of the hard gamma radiation of mesothorium.

The Radioactivity Section of the National Bureau of Standards, Washington, D.C. offers for sale a series of radium gamma-ray standards consisting of 5 ml of radium solution sealed in glass ampoules. These have a radium content varying from 0.1 to 100 micrograms.

3. The Emanation Method of Radium Assay. An extremely sensitive method for the measurement of low intensity samples is the emanation method. In this method the gaseous radon in equilibrium with a radium sample is removed and placed inside an ionization chamber as part of the gas filling. The alpha particles of radon and of its short-lived alpha emitting daughters RaA, and RaC' are heavily ionizing and a small number of disintegrations per minute cause a readily detectable effect. The radon from $10^{-9}$ grams of radium can be measured with ease; with care the radon from $10^{-11}$ grams of radium can be measured. If the individual alpha particles are counted, as little as $10^{-14}$ grams of radium can be so detected.

The slightly-acidic radium solution to be assayed is boiled for several minutes to expel radon and is then sealed for one month to allow radon to come to equilibrium. The solution is then boiled to expel radon; the radon is collected and passed into the ion chamber or electroscope. The rate of leakage of the electroscope is compared with that caused by the radon from a standard solution of radium. This standard solution can be made by taking a very small aliquot of a solution of a radium salt originally standardized by the gamma-ray method. Another type of standard which can be used is a sample of pitchblende with an accurately known content of uranium.

The emanation method can also be used to assay samples for ThX or RnTh content. In this case the thoron daughter is removed and counted. The method must be modified suitably because of the 51 second half-life of the thoron.

4. The Calorimetric Method of Radium Assay. The amount of radium in a sample may be determined by measuring the heat released by the absorption of the energetic radiations within a suitable calorimeter. This is an absolute method and often has several advantages over the gamma-ray comparison method. The $\alpha$, $\beta$ and $\gamma$ radiations of radium and its daughters are sufficiently well known that this heat release can be calculated to better than 0.5 percent. Most of the energy is in the form of the kinetic energy of the alpha particles and the recoil energy from the alpha emission process. This energy is precisely known and is completely released within the calorimeter. The beta particles and conversion electrons are absorbed nearly completely in the calorimeter. The absorption of gamma-radiation is not so easy to compute but since it contributes only about 9 percent to the total heat effect an
error of a few percent in estimating its heat contribution does not affect the overall result to this extent. The uncertainty in the gamma-contribution can be reduced by using a so-called $\beta$-calorimeter i.e., a thin-walled calorimeter in which $\gamma$-absorption is slight. Table 6.8 taken from a paper by GORSHKOV and SHIMANSKAYA\textsuperscript{34} lists the total energy release from an average disintegration of Ra\textsuperscript{226} in equilibrium with its decay products through RaC, RaC\textsuperscript{1} and RaC\textsuperscript{2}. A radium sample which is old enough to have appreciable amounts of 19.2 year RaD (plus RaE and RaF) will have an additional heat contribution from these nuclides. The calorimetric assay method is also useful for mesothorium, radiothorium and actinium as indicated in the table. It is perhaps particularly important for actinium because the weak radiations of Ac\textsuperscript{227} make it particularly difficult to assay by other methods.

International Radium Standards. In 1910 the Congress of Radiology and Electricity appointed a committee to make arrangements for the preparation of an International Radium Standard. Mme. CURIE prepared a sample of 21.99 milligrams of pure radium chloride (August 1911) which was accepted as this standard and arranged that it be located in the Bureau International des Poids et Mesures at Sevre, near Paris. This sample was carefully compared by the gamma-ray balance methods with similar standards prepared by HÖNIGSCHMID for his atomic weight determinations. One of HÖNIGSCHMID'S preparations, containing at that time 31.7 milligrams of radium chloride, was selected by the Vienna Academy of Sciences as a secondary standard. Duplicate standards have been prepared by comparison with the Vienna and Paris standards using the gamma-ray method. In the use of such standards it is necessary to allow for the decay of the radium which occurs at the rate of 0.043 percent per year.

Radon. Radium emanation was discovered by E. DORN in 1900. The name radon, first suggested by C. SCHMIDT, was originally applied only to the emanation of the radium decay chain. Later the name radon came to be used for element 86 and all of its isotopes. An alternate name for the element is emanation, symbol Em.

\textsuperscript{34} See reference 9 in Table 6.7.
Table 6.8 Average Radiation Energies Emitted in Single Disintegrations by Equilibrium Preparations of Radium, Mesothorium, Radiothorium and Actinium and the Heat Effects, \( q \), of the Corresponding Sources with Activities of one Curie.

<table>
<thead>
<tr>
<th>Preparation</th>
<th>( E_{\alpha+\beta} )</th>
<th>( E_{\alpha+\beta+\gamma} )</th>
<th>( q_{\alpha+\beta} )</th>
<th>( q_{\alpha+\beta+\gamma} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra**</td>
<td>25,350</td>
<td>27,140</td>
<td>129.3</td>
<td>138.4</td>
</tr>
<tr>
<td>MsTh</td>
<td>33,920</td>
<td>36,510</td>
<td>173.0</td>
<td>186.2</td>
</tr>
<tr>
<td>RdTh</td>
<td>33,390</td>
<td>35,060</td>
<td>170.3</td>
<td>178.8</td>
</tr>
<tr>
<td>Ac</td>
<td>33,690</td>
<td>34,210</td>
<td>172.0</td>
<td>174.4</td>
</tr>
</tbody>
</table>

From G.V. Gorshkov and N.S. Shimanskaya, Soviet Journal of Atomic Energy, 1956. These authors later revised the radium figures slightly to 138.9 ± 0.7 cal/hr. See Atomnaya Energ. 6, 474 (1959) or Soviet J. Atom. Energ. 6, 339 (1960).

* The value \( E_{\alpha+\beta} \) includes the energy of the recoil atoms, the conversion electrons and the x-radiation.

** No allowance is made for RaDEF which would be present in aged radium samples.
The growth of radon into an initially-pure sample of radium is shown above in Fig. 6.7.

Some recent determinations of the half-life of radon are the following:

- J. ROBERT\textsuperscript{35} \(3.825 \pm 0.004\) days
- J. TOBAILEM\textsuperscript{36} \(3.825 \pm 0.005\) days
- P.C. MARIN\textsuperscript{37} \(3.8229 \pm 0.0027\) days

The energy of the principal alpha particle group of radon was reported as 5.486 MeV by BRIGGS\textsuperscript{38} in 1936. In 1953 BASTIN-SCOFFIER and SANT'ANA-DIONISIO\textsuperscript{16} reported the slightly lower value of 5.482 MeV based on a value of 7.685 MeV for the alpha particle of Po\textsuperscript{214}. WALEN and BASTIN\textsuperscript{18} recomputed this result using WHITE's\textsuperscript{39} value of 5.3054 MeV for Po\textsuperscript{210} and using slightly different corrections for absorption in the source. They report a corrected result of 5.490 MeV. WALEN and BASTIN\textsuperscript{18} applied advanced techniques of low background alpha spectroscopy to detect complex structure in the spectrum of radon. Their results are summarized in the table. The second of these groups had been predicted by the gamma ray measurements of MADANSKY and RASSETTI\textsuperscript{40} who had found a 510 keV gamma ray in 0.07 percent intensity.

### Alpha Groups of Radon

<table>
<thead>
<tr>
<th>Particle Energy (MeV)</th>
<th>Energy of Excited State (keV)</th>
<th>Intensity</th>
<th>Hindrance Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.490</td>
<td>0</td>
<td>~100</td>
<td>0.95</td>
</tr>
<tr>
<td>4.987 ± 0.001</td>
<td>512</td>
<td>7.8 \times 10^{-2}</td>
<td>0.46</td>
</tr>
<tr>
<td>4.827 ± 0.004</td>
<td>675</td>
<td>\textasciitilde 5 \times 10^{-4}</td>
<td>\textasciitilde 0.03</td>
</tr>
</tbody>
</table>

From WALEN and BASTIN\textsuperscript{18}

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THE ACTIVE DEPOSIT OF RAPID CHANGE

General Comments. Any surface exposed to radon gas becomes coated with an invisible deposit of radioactive matter known as the active deposit. It is convenient to discuss separately the active-deposit-of-rapid-change consisting of the products RaA, RaB, RaC, RaC' and RaC", of which the longest-lived is 26.8 minute RaB, and the active-deposit-of-slow-change consisting of 22-year RaD and its descendants RaE and RaF. The active-deposit-of-rapid-change is diagrammed in Fig. 6.9.

To prepare a sample of the active deposit it is necessary only to expose a disc or wire to radon in a suitable vessel. Exposures of a few seconds or minutes duration yield pure Radium A while exposures of 4.5 hours or longer give the equilibrium mixture of products. When the radon gas is pumped away small traces of radon may still be occluded on the surface. The active disc can be washed in alcohol and heated lightly to remove this occluded radon. The RaA daughter product is positively charged at the instant of disintegration of the parent radon atom and can be attracted preferentially to a negatively-charged wire or surface. This technique allows the preparation of highly concentrated and localized sources of the active deposit. It is also possible to freeze radon on a cooled surface upon which it is desired to locate the active deposit. The active deposit may also be prepared by compressing radon into a tube of small volume; later when the radon has been pumped away the deposited activity can be removed from the walls of the tube by rinsing them with hydrochloric acid.

The rate of growth and decay of the various components of the active deposit for different times of exposure to radon is of some importance. Quantitative information is presented in Figs. 6.10, 6.11 and 6.12. Detailed information on the radiation of the individual members of the active deposit is summarized in the discussion below. References to research papers published before 1958 containing more detailed data can be found in the data compilation of STROMINGER, HOLLANDER and SEABORG. 41

Fig. 6.9. Decay scheme of the active deposit of rapid change. Details of the complex radiations are not shown. The total disintegration energy of each mode of decay is given in MeV.
Fig. 6.10. Activity changes in RaA sample prepared by briefly exposing a surface to radon and quickly removing radon; i.e., initial sample is essentially pure RaA. Growth and decay of RaA (Po$^{218}$), RaB (Pb$^{214}$), RaC(Bi$^{214}$) and RaC' (Po$^{214}$).
Fig. 6.11. Growth of RaA, RaB, RaC, and RaC" into an initially pure sample of radon. Radon not removed.
Fig. 6.12. Activity changes in active deposit prepared by exposing a surface to radon for a sufficient time (~ 4.5 hours or longer) to achieve equilibrium, and then removing radon.
The active deposit can be chemically fractionated so that the individual activities can be separately studied. Separation of RaB and RaC and examination of the radiations and decay characteristics of the separated samples played a prominent role in the original determination of the course of the decay chain. Pure samples of 26.8-minute RaB (Pb 214) may readily be prepared by recoil from RaA. A negatively-charged plate is placed above a sample of RaA, preferably in a vacuum. A considerable fraction of the RaB atoms are ejected from the source plate during the energetic alpha decay of RaA and are collected. RaC grows into such samples but the radiations of RaB predominate for some minutes and can be clearly distinguished.

Pure samples of RaC (Bi 214) can be prepared by the recoil technique using as a source the RaB present in the active deposit from radon after the RaA has completely decayed. However, the yield is quite low because RaB is a beta emitter and the recoil energy is small. However, by various chemical techniques RaC can be separated cleanly from RaB. Samples of RaC do not remain pure because the principal decay product, RaC' (Po 214), grows into equilibrium virtually instantaneously; also the branch product RaC'' (Tl 210) grows into equilibrium within 10 minutes.

The half-life of RaC'' (Tl 210) is very short but by working quickly with intense sources of active deposit is is possible to isolate pure samples for study of the radiations. It is possible to isolate RaC'' by alpha recoil from samples of RaC. In spite of the small alpha branching of RaC (0.04%) it is possible to prepare pure samples because the main-line decay product, RaC', is collected with very low efficiency and furthermore decays completely within one second. HAHN and MEITNER (1909) and FAJANS (1911) first studied samples of RaC'' prepared by the recoil method and established the existence of the branching decay of RaC. This was the first case of branching decay to be established clearly.

Radium A and Its Rare Branch Product, At 218. Radium A decays more than 99% by the emission of 6.002 MeV alpha particles. In 10⁻³ percent

42. G.H. Briggs, Proc. Roy. Soc. (London) 157A, 183 (1936); M.G. Halloway and M.S. Livingston, Phys. Rev. 54, 18 (1938). The alpha particle energy quoted in these earlier references is 5.998 MeV.

of the alpha disintegrations a lower energy group with energy 5.182 MeV is emitted. In addition, Radium A is unstable with respect to At$^{218}$ by about 0.4 MeV so that some branching decay by beta emission might be expected. With this decay energy and the most favorable beta transition (allowed, log $\tau$ = 5) the beta branching could be as large as one percent.

KARLIK and BERNERT proved the existence of this branching decay. By examining the alpha particle groups emitted from freshly-deposited radium active deposit, they were able to observe alpha particles of 6.72 MeV energy. These were observed to grow into the RaA sample with a half-life of a few seconds. From the later work of WALEN and of HIESSBERGER and KARLIK the best value for the half-life of At$^{218}$ is about 2 seconds and the branching ratio of RaA is $2.1 \times 10^{-4}$. In all cases the alpha energy measurements were made with an ionization chamber. These results have been confirmed very satisfactorily by the beautiful alpha spectra obtained by WALEN and BASTIN. These workers remeasured the alpha spectra of radium and its alpha-emitting daughters by new techniques of low-background alpha spectroscopy in a magnetic spectrometer of high precision. In their spectra they were able to resolve clearly the main alpha group of At$^{218}$ for which they determined the energy $6.6975 \pm 0.003$ MeV. A tentative assignment was made of a second group with energy $6.653 \pm 0.005$ MeV in one-sixteenth the intensity of the main group. The branching of RaA to produce At$^{218}$ was set at $1.85 \times 10^{-4}$ in excellent agreement with the previous work. The decay scheme of At$^{218}$ is further discussed by WALEN and BASTIN-SCOFFIER.

The Decay of Radium B. This nuclide decays 100 percent by $\beta$ emission. The $\beta$ and $\gamma$ spectra are complex and the decay scheme is not completely fixed or interpreted. A partial decay scheme is shown in Fig. 6.13 based largely

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*In Table 4.1 of Chapter 4 the alpha energies of the At$^{218}$ groups are listed 12 keV lower because in that table the Briggs value of 6.775 MeV for the Po$^{216}$ (ThA) alpha standard is used whereas Walen and Bastin used the value 6.787 MeV for Po$^{216}$.

Fig. 6.13. Partial decay scheme of Radium B ($\text{Pb}^{214}$).
on the work of Nielsen, Nielsen and Waggoner\textsuperscript{48} and of Kageyama.\textsuperscript{49} Wahlen and Bastin-Scoppier\textsuperscript{47} also comment of the decay scheme of Pb\textsuperscript{214}. Table 6.9 lists several determinations of the gamma rays of Radium B. The beta spectrum has been resolved into several components. Berlovich\textsuperscript{50} reports a main group with 0.73 MeV endpoint energy and a second at 0.67 MeV with relative intensities 100 to 33. Kageyama\textsuperscript{49} resolves out one component at 0.59 MeV and a second at 0.65 MeV with 56 and 44 relative intensities. Daniel\textsuperscript{51} resolves a ground state beta transition with energy 1.03 MeV in 6 percent intensity.

Long Range Alpha Particles of Radium C'. Two modern measurements of the short half-life of Po\textsuperscript{214} (Ra'C') by the delayed coincidence technique gave the results $1.64 \times 10^{-4}$ and $1.58 \times 10^{-4}$ seconds, respectively.\textsuperscript{52,53} Polonium\textsuperscript{214} decays entirely by alpha particle emission. More than 99 percent of the decays are ground-state-to-ground-state transitions with an energy given as 7.680 MeV in the classic work of Briggs\textsuperscript{42} and as 7.683, 7.685 or 7.687 MeV in more recent determinations.\textsuperscript{54,55,55a} A second group at 6.905 MeV in the low intensity of $10^{-2}$ percent has also been reported.\textsuperscript{43}

The alpha spectrum of RaC is characterized by the presence of low-intensity alpha particles of very long range which originate in the following way. The beta branching decay of RaC is complex and results in the production of RaC' daughter atoms in a large number of excited states. These excited levels de-excite to the ground state of RaC' by gamma-ray emission or by a gamma-ray cascade. However, in an appreciable fraction of cases these excited levels are partially de-excited by alpha-particle emission to the ground state of Pb\textsuperscript{210}. The alpha-particles are greater in energy than the ground-state-to-ground-state transition energy. This phenomenon of observable alpha

\textsuperscript{54} W.J. Sturm and V. Johnson, Phys. Rev. 82, 542 (1951).
### Table 6.9 Gamma Rays of Radium B (Pb$^{214}$)

(Energy in keV)

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<td>53</td>
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</tr>
<tr>
<td></td>
<td>206</td>
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<tr>
<td>241.92 (20)</td>
<td>242 (6.7)</td>
<td>241.9 Ml</td>
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<td></td>
<td>259</td>
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<tr>
<td></td>
<td>272 (weak)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>275</td>
<td></td>
</tr>
<tr>
<td></td>
<td>279 (weak)</td>
<td></td>
</tr>
<tr>
<td>295.22 (55)</td>
<td>295 (15.9)</td>
<td>295.2 Ml</td>
</tr>
<tr>
<td>352.0 (100)</td>
<td>352 (31.6)</td>
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<tr>
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<td>481</td>
<td></td>
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<tr>
<td></td>
<td>534</td>
<td></td>
</tr>
<tr>
<td></td>
<td>549 (weak)</td>
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<tr>
<td></td>
<td>777</td>
<td></td>
</tr>
</tbody>
</table>

Relative intensities are given in parentheses.

Ref. 1 Muller, Hoyt, Klein and DuMond, Phys. Rev. 88, 775 (1952). These precise values were measured in a crystal spectrometer.

Ref. 2 Nielsen, Nielsen and Waggoner, Nuclear Physics 2, 476 (1957).

Ref. 3 M. Mladjenovic and H. Sltis, Arkiv Fysik 8, 65 (1954).

NOTE: In the classical literature a special nomenclature was used for the $\gamma$-transitions of the active deposit. In Ellis' notation (Proc. Roy. Soc. 143A, 350 (1933) the 242, 295 and 352 keV transitions were called F, G and H.
branching of an excited level in competition with gamma emission is a very rare occurrence. Among the naturally occurring activities only ThC' shows similar long-range alpha particles. The reason such branching appears in these particular instances is that the alpha decay energy available is so very great.

Table 6.10 lists twelve long-range alpha groups assignable to RaC'. A large number of gamma-rays are observed in the decay of RaC and many of these correspond to transitions between the energy levels from which alpha decay is occurring. See discussion below.

Decay of Radium C. The 0.021 percent alpha branching of Radium C will be mentioned first as our knowledge of this decay can be more quickly summarized. The most complete study of the alpha spectrum was made by WALEN and BASTIN-SCOFFIER55 with the results summarized in Table 6.11.

The beta decay energy of Radium C is 3.26 MeV56 and the number of energetic beta and gamma rays emitted in the course of the decay is quite large. Sixty gamma rays have been reported and more than forty of these are above 1 MeV in energy. About ten percent of the beta transitions lead to levels in Po214 lying 2.4 MeV or higher in energy so that the intensity of many of the high energy gamma rays is high. Most of the high energy radiation associated with radium and radium preparation is attributable to the radium C present in these preparations.

These radiations have been studied by a variety of experimental techniques, but it would require too much space to summarize the numerous published works in any detail. MAYER-BÖRICKE57 has published a very extensive paper which summarizes his own findings and those of most other authors in publication by 1959. We reproduce here a long table (see Table 6.12) from this article which summarizes published information on the gamma transition

57. C. Mayer-Böricke, Z. Für Naturforschung, 14a, 609 (1959); for an extension of this study see references 57a and 57b.
Table 6.10 Long Range Alpha Groups from RaC\textsuperscript{1} from (W.B. Lewis and B.V. Bowden, Proc. Roy Soc. (London) \textbf{145}A, 235 (1934); G.H. Briggs, Rev. Modern Phys. \textbf{26}, 1 (1954)).

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<tr>
<th>Energy of alpha particle (MeV)</th>
<th>Energy of disintegration (MeV)</th>
<th>Difference of Energy of disintegration from main group (MeV)</th>
<th>Relative number of alpha-particles</th>
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<td><strong>Main Group</strong></td>
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<td>7.680</td>
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<td>0</td>
<td>10\textsuperscript{6}</td>
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<td><strong>Long Range Groups</strong></td>
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<td>8.277</td>
<td>8.437</td>
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<td>8.938</td>
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<td>1.283</td>
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<td>9.313</td>
<td>9.493</td>
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<td>9.673</td>
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<td>9.657</td>
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<td>10.146</td>
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<td>10.506</td>
<td>10.709</td>
<td>2.880</td>
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\textsuperscript{†} The energy of the main group has been redetermined as 7.685 MeV by Walen and Bastin\textsuperscript{43} (1958); as 7.687 by Rytz\textsuperscript{55a} and as 7.683 by Sturm and Johnson.\textsuperscript{54}
Table 6.11 Alpha Spectrum of Radium C (Bi$_{214}^4$)

Walen and Bastin-Scoffier, Nucl. Phys. 16, 246 (1960)

<table>
<thead>
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<th>Energy* (MeV)</th>
<th>Relative Intensity</th>
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<td>5.448</td>
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<td>5.184</td>
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<td>5.023</td>
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<td>4.941</td>
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* Measured relative to $E_\alpha$ (Po$_{210}^4$) = 5.304 MeV.

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<th>Ref.</th>
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<tr>
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Notes on Table:
Energies are given in MeV. If the intensity of the gamma ray was reported in the cited article it is given directly underneath the energy value; the numbers are relative to the 2.204 MeV line. Energy values in parentheses were taken over from other authors.
Table 6.12 (Cont'd)

**KEY TO Methods used:**

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<tr>
<td>sπ</td>
<td>magnetic 180° spectrometer</td>
</tr>
<tr>
<td>sπ√2</td>
<td>magnetic double focusing spectrometer</td>
</tr>
<tr>
<td>sl</td>
<td>magnetic</td>
</tr>
<tr>
<td>ph</td>
<td>photographic recording</td>
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<tr>
<td>gm</td>
<td>Geiger-Müller counter recording</td>
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<td>scin pr</td>
<td>scintillation pair spectrometer</td>
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<td>scin</td>
<td>single crystal scintillation spectrometer</td>
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<tr>
<td>Dγp</td>
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<td>Cpt e⁻</td>
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The chief methods employed in the cited publications were the following:

- conversion electrons I-VI; external conversion VII - XI, photoproton energy in deuterium-filled counter XII, Compton distributions XIII-XIV; Compton line method XV-XX and scintillation pair spectrometer XXI.
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<td>2, Supple. 1</td>
<td>54</td>
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</table>
energies and intensities. Over the years many authors\textsuperscript{57-69} have constructed partial decay schemes showing the placement of the most intense radiations. Some of the older versions of the decay scheme have had to be discarded because of incompatibility with later measurements of $\gamma$\textsuperscript{62,64,65} or $\beta$ $\gamma$ cascades.\textsuperscript{63,67} We reproduce here as Fig. 6.14 the decay scheme published by LUHRS and BORICKE.\textsuperscript{57a} Without going through the detailed justification of this scheme we wish to call attention to a few important considerations in its construction.

Firstly, the numerous long-range alpha particles of Radium C' (summarized in Table 6.10 above) are extremely helpful in constructing a level skeleton. Under the assumption that each of these long-range groups goes to the ground state of Pb\textsuperscript{210} one deduces a set of levels in Bi\textsuperscript{214} which are identical with those listed in the third column of Table 6.10. This assumption turns out to be correct for all but three of the long-range alphas; in the case of alpha particles with 9.313, 9.779 and 9.905 MeV energy HAUSER\textsuperscript{69} has presented arguments proving that these events must terminate in excited levels in Pb\textsuperscript{210} at 0.778 or 1.077 MeV.

The fact that most of the long-range alpha transitions do terminate in the O$^+$ ground state of Pb\textsuperscript{210} helps to fix the spin and parity of the RaC'
Fig. 6.14 Decay Scheme of Radium C as drawn by Lührs and Mayer-Böricke. Energies of β groups are given in MeV, the γ-energies in keV. The long range alpha groups originating from the excited levels of Radium C' are shown as slanting arrows at the left end of the levels. γγ coincidence measurements are indicated by dots at the tips of the arrows which indicate the γ-transition to the RaC' level common to the two coincident γ-transitions. Figure reproduced from Z.f. Naturforsch, 15A, 939 (1959).
levels. Since alpha transitions can remove only even units of angular momentum in combination with positive parity or odd units of angular momentum in combination with odd parity, the Radium C' levels are restricted to 0+, 1-, 2+, 3-, 4+, ... From the γ-transition data and from the alpha decay probabilities the range of possible assignments can be further reduced to 0+, 1- or 2+.

Multipolarity assignments of M1 or E2 have been made to several of the prominent transitions chiefly by measurement of conversion electron ratios. See particularly the work of Nielsen, Nielsen and Waggoner 70 and of Lührs and Mayer-Börnicke. 57a These assignments help in fixing the spin and parity assignments of several levels. One important transition with 1.416 MeV energy is identified with certainty as an E0 transition by the prominence of its conversion electrons and absence of gamma ray photons; this fixes the spin of the 1.416 level as 0+. Tutter 71 has measured the half-life of this level as 2.3 x 10−10 seconds. There is evidence 57 for an additional E0 transition in the decay of the level at 2.510 MeV to ground so this level also is designated 0+. All the other levels from which long-range alpha particles are emitted also are de-excited to the ground state of RaC' by the emission of gamma ray photons; this fact eliminates 0+ as a possible assignment and fixes the assignments as either 1- or 2+.

A number of the prominent levels below 2.5 MeV are placed with the help of γγ and βγ coincidence results of several workers; 62-65,67 some of these measurements are summarized in the decay scheme by the dots, as explained in the figure caption. Above 2.5 MeV the level scheme is based chiefly on two types of evidence. The first is an analysis by Hauser 69 of the pattern of alpha emission of the longest-range alpha particles. The second is the measurement 57 of many new energetic gamma rays lying above 2.6 MeV. Since the total decay energy is 3.26 MeV and the first excited state is 0.609 MeV the most energetic gamma rays cannot be in coincidence with any of the gamma rays of lower energy and hence must represent direct transitions to ground. This fixes the positions of a number of the highest-lying levels.

Many authors have published analyses of the complex beta spectrum but these reports are discordant. The analysis by DANIEL and NIERHAUS was used by MAYER-BÖRICE in the construction of Fig. 6.14. The possibility that the beta rays groups are still incompletely resolved is recognized and is represented in the figure by brackets which group the levels which may be fed by each partially resolved beta group.

There exists no theoretical interpretation of the complex level scheme of Po. Mayer-Boricke discusses the possibility that the lowest levels of excitation may represent collective quadrupole vibrations of the entire even-even Po nucleus about its spherical equilibrium shape. The pattern of the gamma ray de-excitation characteristics follows closely the pattern for such collective vibrations first pointed out by SCHARFF-GOLDBHABER and WENESER. These vibrations are discussed in Chapter 3. The characteristic features are a first excited 2+ state de-excited by an E2 transition with greatly enhanced transition probability and a second excited state lying at \( \sim 2.2 \) times the energy of the first; this second excited state has 2+ character (although according to some theories it may have 0+, 2+, 4+ triplet character), an enhanced E2 transition probability for a transition to the first excited state, and negligible probability for a direct transition to ground. In the case of Po the 2+ level at 609 keV and the 2+ level at 1.378 MeV seem to fit these characteristics. Lührs and Mayer-Boricke measured the K/L ratios of the 609 and 769 keV radiations and characterized them as very pure E2 radiations. They discussed the level system of Po in terms of the theoretical model of WILETS and JEAN.

Decay of Radium C'' (Thallium-210). This rare branch product has a half-life of 1.3 minutes for beta decay. From a closed decay-energy cycle the decay energy of Tl is estimated to be 5.47 \( \pm 0.04 \) MeV. The end point

77a. L. Wilets and M. Jean, Phys. Rev. 102, 788 (1956).
energy of the beta particles is 1.96 MeV showing that the beta decay selects a very high-lying level (~3.5 MeV) in the Pb$^{210}$ daughter nucleus. Good agreement on the beta energy has been obtained by several authors using different techniques: LECOIN$^{78}$ reports 1.95 MeV based on a cloud chamber method; DEVONS and NEARY$^{79}$ find 1.95 ± 0.15 MeV by an absorption technique; MAYER-KUCKUK$^{80}$ obtains 1.96 ± 0.1 MeV and STETTER$^{80a}$ obtains 1.97 ± 0.05 MeV by scintillation spectrometer measurements.

The most detailed study of the radiations of Radium C" was made by STETTER. The short half-life and, in particular, the slight alpha branching of Radium C make it almost impossible to prepare intense sources. Hence the radiations had to be studied with scintillation counters of high efficiency but low resolution. By pushing scintillation techniques to the limit and overcoming many experimental difficulties in sample preparation STETTER succeeded in resolving the many gamma rays listed in the accompanying table. $\beta\gamma$ and $\gamma\gamma$ coincidence results helped him to formulate the decay scheme shown in the figure.

It is seen that nearly all beta transitions populate a few levels above 3.5 MeV which are de-excited through a series of parallel $\gamma$-ray cascades, all of which funnel through a 2+ level lying at 790 keV of excitation. The total decay energy is 5.5 MeV.

It is of interest to compare the experimental level scheme of Pb$^{210}$ seen in the decay of Tl$^{210}$ with the predictions of shell model theories. Lead-210 has just 2 neutrons more than the closed shell nucleus Pb$^{208}$ so that it is a very favorable case for a shell model calculation of the level system. In principle one starts with the neutron wave functions predicted by theory for $N > 126$ and the energies of neutrons in these states as observed in the Pb$^{209}$ nucleus. One considers all possible combinations of 2 neutrons in the available states and computes the energy of these combinations from the sum

80a. G. Stetter, unpublished report of work at Physical Institute of the University of Vienna, TID-14880 (1961).
of the energies of the individual orbitals reduced by the energy of the residual interaction between the two neutrons. PRYCE, MAYER-KUCKUK and STEITTER have outlined how such a calculation is carried out and have shown what form the theoretical spectrum might take. The weak point in these tentative calculations is the uncertainty of the shell model assignment of the neutron levels of Pb\(^{209}\), particularly in view of the later work of MUKHERJEE and COHEN.

The shell model interpretation of the Tl\(^{210}\) nucleus is an \(s_{1/2}\) proton hole state combined with 3 neutrons in \(g_{9/2}\) states—all coupled to \(4^+\) or \(5^+\).

The decay of RaC\(^{\prime\prime}\) has the interesting feature that the total beta-decay energy (5.4 MeV) to produce Pb\(^{210}\) is greater than the neutron binding energy (4.81 MeV) of Pb\(^{210}\). KINSEY, BARTHOLOMEW and WALKER pointed out that this suggests the possibility that neutrons may be emitted in the disintegration of RaC\(^{\prime\prime}\) provided some of the beta transitions lead to excited states above the neutron binding energy. These authors looked for such neutrons from commercial sources of radium in equilibrium with their products and were unable to detect any neutrons other than those to be expected from \((\alpha, n)\) reactions on light element impurities in the container or the sample. On the other hand KOGAN and RUSINOV have obtained neutron counting data on the active deposit of radium emanation which indicates rather clearly that neutrons are indeed emitted in the decay of radium C\(^{\prime\prime}\). They estimate the number as \(2 \times 10^{-4}\) per disintegration. STEITTER confirms this by direct measurement of neutrons from a radium C\(^{\prime\prime}\) sample.

---

Figure showing decay scheme of Radium C'' as formulated by Stettler. This is a tentative scheme as there is not clear experimental proof of the placement of some of the gamma rays.
### Gamma Rays Emitted in the Decay of Radium - C" (Thallium-210)

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Mayer-Kuckuk</th>
<th>P. Weinzierl</th>
<th>Stettler</th>
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<td>Energy (keV)</td>
<td>Intensity %</td>
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</tr>
<tr>
<td>21</td>
<td>2460</td>
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</table>

THE ACTIVE DEPOSIT OF SLOW CHANGE

General Comments. When radon samples or high-intensity samples of the active deposit are permitted to decay there always remains a residual long-lived activity after the radon and the active-deposit-of-rapid-change has decreased below the detectable limit. This residual activity is the radium D-E-F Complex, at one time referred to as the active-deposit-of-slow-change.

\[
\text{RaD}(\text{Pb}^{210}) \xrightarrow{\beta^-} \text{RaE}(\text{Bi}^{210}) \xrightarrow{\beta^-} \text{RaF}(\text{Po}^{210}) \xrightarrow{\alpha} \text{RaG}(\text{Po}^{206}) \text{STABLE}
\]

Radium D is identical with the radiolead first reported by HOFFMANN and STRAUSS in 1901. Radium F is identical with the radioelement polonium, found by the CURIES in 1898. We summarize recent determinations of the properties of these important nuclides in the following paragraphs. Numerous references to older measurements of these radiations are cited in the compilation of STROMINGER, HOLANDER and SEABORG. 85

Radium D (Pb\textsuperscript{210}). Modern determinations of the Radium D half-life include those of TOBAILEM 86 (measurement of decay over 4 month period by dual ion-chamber technique leading to the result 19.4 ± 0.35 years), of HARBOTTLE 87 (measurement of decay over 280 day period by dual ion-chamber technique leading to the result 20.4 ± 0.3 years) and of ECKELMANN, BROECKER and KULP 88 (a geological method consisting of the isolation of lead from an undisturbed uranium mineral and the determination of the Pb\textsuperscript{210} content from Po\textsuperscript{210} in equilibrium with it, leading to a Pb\textsuperscript{210} half-life of 21.4 ± 0.5 years).

The beta particles of Radium D are very weak and consist of two groups. 89,90 The weaker group is in 15 percent intensity and has an end point

energy of 64 keV; it represents the ground state transition. The stronger
group is in 85 percent intensity and has an end point energy of only 17 keV.
Careful techniques of sample preparation and counting are required to detect
these low-energy beta particles. This beta group is followed by an M1 gamma
transition of 46.7 keV energy which is almost completely converted. No other
gamma rays are present.91

For many years it was suspected that Radium D must emit alpha particles
in a small fraction of its disintegrations. But because of the slight magni-
tude of this branching and the unknown properties of the Hg\textsuperscript{206} daughter it was
difficult to obtain evidence for this mode of decay. This evidence was eventu-
ally obtained by the Finnish scientists, NURMIA and CO-WORKERS\textsuperscript{91a} who
measured alpha particles of approximately 3.7 MeV and isolated and identified
the Hg\textsuperscript{206} daughter, which proved to be an 8.6 minute beta-emitter. The alpha
branching is only \(1.8 \times 10^{-8}\) corresponding to a partial alpha half-life of
\(10^9\) years.

Radium E (Bi\textsuperscript{210}). A recent careful redetermination of the half-life
of Radium E yielded the value \(5.013 \pm 0.005\) days.\textsuperscript{92} Among the most careful
work on the beta spectrum is that of PLASSMANN and LANGER\textsuperscript{93} who report the
value 1.155 MeV for the maximum energy. The beta decay goes directly to the
ground state of Radium F and no gamma radiation is detected. Radium E also
decays to Tl\textsuperscript{206} by alpha emission but the alpha branching is only \(5 \times 10^{-5}\)
percent.\textsuperscript{94} This alpha branching is discussed in detail below in connection
with the discussion of the isomeric forms of Bi\textsuperscript{210}.

\textsuperscript{91}. A discussion of all measurements of the gamma radiations in the decay of
radium D and radium E is given by Pink, Warren, Edwards and Danon, Phys.
Rev. \textbf{103}, 651 (1956).


Radium F ($^{210}\text{Po}$). Two modern determinations of the Radium F half-life are those of CURTIS\cite{95} and of EICHELBERGER, JORDAN, ORR and PARKS\cite{96} who reported 138.37 ± 0.03 days and 138.4005 ± 0.0058 days, respectively.

Polonium 210 is a pure alpha emitter whose alpha spectrum contains a single alpha group which populates directly the ground state of Pb$^{206}$ so that no gamma radiation accompanies the decay. This statement must be qualified slightly because 803 keV gamma radiation does occur in an intensity of (1.06 ± 0.02) per 10$^5$ disintegrations.\cite{98} This observation indicates a very slight alpha branching to an 803 keV level in Pb$^{206}$ which decays by emission of electric quadrupole radiation.

FENYES\cite{96a} has made a direct measurement of the energy of this weak alpha group in a magnetic spectrometer whose alpha detector was gated with pulses from a gamma detector placed back of the source. He reports an energy of 4.525 ± 0.05 MeV corresponding to an energy of 795.6±5 keV for the excited state of Pb$^{206}$.

Polonium 210 is widely used for a variety of purposes for which a long-lived alpha emitter, unaccompanied by gamma radiation, is needed. It is also widely used as a standard in alpha particle spectroscopy so that the value of its alpha particle energy is a matter of considerable importance.

The energy of the Po$^{210}$ alpha particle has often been measured relative to the main alpha group of RaC' for which BRIGGS\cite{97} has measured an absolute value with great accuracy. LEWIS and BOWDEN\cite{97a} calculate an absolute value of 5.299 MeV for Po$^{210}$ from a consideration of several measurements of the RaF to RaC' energy ratio. Many published alpha particle energies in the translead region are based directly or indirectly on this value of the Po$^{210}$ alpha particle as a standard. Some recent direct determinations of the Po$^{210}$ alpha particle energy have given values a few kilovolts higher. These newer

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Recent Absolute Measurements of the Polonium 210 Alpha Particle Energy
(Table prepared by F. Asaro*)

<table>
<thead>
<tr>
<th>Value</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3086 ± 0.003</td>
<td>Browne, Galey, Erskine and Warsh, Phys. Rev. 120, 905 (1960).</td>
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<tr>
<td>5.3028 ± 0.0010</td>
<td>Wapstra*</td>
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</tbody>
</table>

* Proceedings of the International Conference on Nuclidian Masses, McMaster University, Canada, September (1960).
Computation of absolute energy of Po$^{210}$ alpha particle from Experimental Measurement of Ratio of Po$^{210}$ and RaC' alpha energies and from Brigg's value of 7.6804 MeV for the main RaC' alpha particle.

<table>
<thead>
<tr>
<th>Energy (MeV)</th>
<th>Author</th>
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<tbody>
<tr>
<td>5.3003</td>
<td>Ryz, Compt. rend. 250, 3156 (1960).</td>
</tr>
</tbody>
</table>
determinations are summarized in the table. On the other hand, if recent
determinations of the ratio of the Po\textsuperscript{210} alpha particle energy to the RaC\textsuperscript{1} alpha particle energy are combined with the accepted Brigg's value for the
RaC\textsuperscript{1} alpha particle one obtains the alternate set of values summarized in
the second table. These values cluster strongly around the old value 5.299
MeV. This strongly suggests that the energy of the RaC\textsuperscript{1} alpha particles as
well as the Po\textsuperscript{210} alpha particle need to be raised a few kilovolts from their
formerly-accepted values. An excellent discussion of remaining difficulties
in the selection of an absolute energy standard is given by G. C. Hanna.\textsuperscript{98a}

Radium D-E-F Radioactivity Standards. A sample of Radium D-E-F makes
a convenient beta-ray standard. The alpha disintegration rate of Radium F
can easily be determined in a suitable alpha counter to an accuracy of 99
percent or better and at equilibrium, the alpha-disintegration rate of Radium
F is equivalent to the beta disintegration rate of Radium E. If the Radium
D-E-F standard is covered with approximately 11 milligrams per square centi-
meter of aluminum absorber the activity detected in a Geiger tube, proportional
counter, or other beta-ray detector is due solely to RaE; the alpha particles
of RaF and the soft beta-particles from RaD are completely absorbed by the
aluminum. The counting rate of such a standard decreases with the 19.40-year
half-life of RaD. Hence with such a standard one has the advantage of the
energetic electrons of the 5-day RaE, uncomplicated by conversion electrons,
gamma radiation, or lower energy beta groups, coupled with the long half-life
of RaD. Such standards are easily made.

The Radioactivity Section of the National Bureau of Standards, Wash-
ington, D.C. offers RaE standards for sale. These standards consist of an
electrolytic deposit of lead containing RaD in the form of PbO\textsubscript{2} on the palla-
dium surface of a palladium-clad silver disk. The lead is separated quanti-
tatively from a high grade pitchblende ore and the RaD activity is calculated
from measurement of the radon in equilibrium with Ra\textsuperscript{226} in the ore.

In connection with the preparation of standards or for other reasons
it is useful to know the growth curves for RaE and RaF into pure RaD. These
are shown in Figs. 6.15 and 6.16. The growth of RaD into pure Ra\textsuperscript{226} is

\begin{footnotesize}
\textsuperscript{98a} G.C. Hanna in "Experimental Nuclear Physics", Vol. III, E Segrè, editor,
\end{footnotesize}
Fig. 6.15. Growth of RaE (5-day Bi$^{210}$) into pure RaD (19.4 year Pb$^{210}$).
Fig. 6.16. Growth of RaF (138-day Po$^{210}$) into pure RaD (19.4 year Pb$^{210}$).
shown in Fig. 6.17.

Theoretical Interest in the Beta decay of Radium E. The shape of the beta spectrum of RaE has been of great interest to beta decay theorists for many years and so has been studied and restudied carefully by many experimentalists. It was the first beta spectrum definitely proved to have a shape differing markedly from the shape characteristic of allowed beta transitions. The spectral shape appeared to correspond to that expected for a twice-forbidden (\(\Delta I = 2\), no change of parity) beta transition. Since RaE decays into the ground state of an even-even nucleus which must have spin 0\(^+\), the spin of RaE was assigned the value 2\(^+\). When the shell model of the nucleus was developed it became clear that RaE could not have even parity. (The odd, 83rd, proton in Bi\(^{210}\) has available to it only the negative parity states \(h_{9/2}, f_{7/2}\) and \(p_{3/2}\); the odd, 127th neutron can only be in the positive parity states \(i_{11/2}, g_{9/2}\) or \(d_{5/2}\). Hence RaE must have odd parity). At a later date the spin of RaE was definitely determined to be 1 by the atomic beam experiments of K. Smith.\(^99\) Hence the theoretical problem became how to account for the non-typical spectrum shape for a transition of the type, \(1^- \rightarrow 0^+\). A satisfactory but not completely convincing fit was obtained by invoking different mixtures of the five fundamental beta coupling components: S, V, T, A and P. The status of the theoretical interpretations of the RaE beta spectrum shortly before the parity conservation law for weak interactions was shown to be invalid is well reviewed by Plassmann and Langer\(^100\) and by C.S. Wu.\(^101\) The theoretical interpretation of the RaE spectrum underwent further changes as theoretical ideas on beta decay interactions were revised subsequent to the discovery of the non-conservation of parity. We shall not review this matter here.

NEWBY and KONOPINSKI\(^102\) carried through an interesting shell model analysis of the character of the ground state of RaE. This analysis is important for the interpretation of the beta decay in that it shows that the

\(^99\) K.F. Smith, as quoted by C.S. Wu in reference 101.


Fig. 6.17. Growth of RaD (19.4 year Pb\textsuperscript{210}) into Ra\textsuperscript{226}.
β transforming neutron of RaE most probably has \( \frac{1}{2} \) character despite a \( \frac{9}{2} \) character of the ground state neutron in Pb\(^{209}\). The calculation is also important in that it reveals the resemblance of the proton-neutron interaction for two nucleons beyond the double closed shell at Pb\(^{208}\) to the mutual interaction of a free neutron and proton. These calculations represent an extension of the calculations of PRYCE and of TRUE and FORD on the level schemes of Pb\(^{206}\), which are reviewed at length in Chapter 10, and which show that the interaction of two neutrons (in this case neutron hole states) in a heavy nucleus can be characterized by a force close to that observed for free neutrons. Other shell model theoretical analyses of the levels of Bi\(^{210}\) are given by SLIV, SOGOMONOVA and Kharitonov,\(^{113}\) by ZEH and MANG,\(^{102a}\) and by KIM and RASMUSSEN. The calculations of the last set of authors is particularly successful in accounting for the \( 1^- \) character of the radium E ground state whereas it might be expected that the \( 0^- \) state would be lowest. As suggested by Newby and Konopinski and confirmed in the calculations of KIM and RASMUSSEN, it is the action of tensor forces between the odd neutron and the odd proton which account for the strong depression of the \( 1^- \) state below its expected position.

The β spectrum of RaE is also of importance in a practical sense in connection with the so-called FEATHER analytical method\(^{103}\) for determining the ranges of beta emitters. Frequently, it is desired to determine the maximum range (hence energy) of an unknown beta emitter or mixture of beta-emitters by noting the reduction in counting rate in a geiger counter or similar detector when various thicknesses of absorber are placed between the sample and the detector. The "visual end-point" is easily determined for a simple beta emitter uncomplicated by gamma radiation, but is hard to estimate with confidence when a mixture of beta emitters or considerable gamma radiation is present. In such cases, a comparison of the shape of the absorption curve of the unknown sample with that of standard substance according to the FEATHER method will reveal the beta range or ranges with more certainty.

\(^{102a}\) H. Zeh and H. Mang, Nuclear Physics 22, 529 (1962).
\(^{102b}\) Y.E. Kim and J.O. Rasmussen, unpublished results (1962).
\(^{103}\) N. Feather, Proc. Cambridge Phil. Soc. 34, 599 (1938).
RaE has frequently been used as the standard substance because it has only a single beta group and no gamma radiation. Details on the application of the Feather method which has been much used in the past, may be found elsewhere.  

Isomerism in Bi$^{210}$. Studies of bismuth isotopes produced artificially have shown the existence of a form of Bi$^{210}$ isomeric with RaE. It will be convenient to discuss this isomerism here.

NEUMANN, HOWLAND and PERLMAN$^{106}$ found that neutron irradiation of bismuth (100% Bi$^{209}$) in a high neutron flux produced a new bismuth alpha-emitter of low activity which could best be assigned to Bi$^{210}$. This work was extended by LEVY and PERLMAN.$^{107}$ The evidence for the mass assignment is very strong and consists of the following:

1. The new radioactivity is produced by irradiation of Bi$^{209}$ with neutrons.

2. The alpha particle energy, 4.935 ± 0.020 MeV (total minimum disintegration energy 5.031 MeV) corresponds to that expected for Bi$^{210}$ and not to that for Bi$^{208}$ or Bi$^{211}$, the only other bismuth isotopes which conceivably could be formed.

3. Daughter activity agreeing in properties with the 4.2 ± 0.5 min.
beta emitter, Tl$^{206}$, could be isolated in about the correct amount.

4. When a sample of bismuth containing the new alpha emitter was subjects to calutron isotope separation the alpha activity was found to concentrate in the mass 210 fraction.

5. The neutron absorption cross-section$^{108,109}$ of Bi$^{209}$ as determined by activation of RaE is 19 ± 2 millibarns whereas the total absorption cross section is 33 ± 2 millibarns. The difference of 14 ± 3 millibarns is attributed to the formation of the long-lived isomer of Bi$^{210}$.

104. L.E. Glendening, Nucleonics 2, No. 1, 12 (1948).
6. Po\(^{210}\) alpha activity has been observed to grow into bismuth samples containing Bi\(^{210}\) (long-lived) long after the RaE had completely decayed.\(^{107}\)

The half-life of Bi\(^{210}\) (long-lived) was calculated by Hughes and Palevsky\(^{108}\) to be \((2.6 \pm 0.8) \times 10^6\) years assuming 14 millibarns for the neutron activation cross section of Bi\(^{209}\) to produce Bi\(^{210}\) (long) and using data of Neumann, Howland and Perlman\(^{106}\) on the specific alpha activity of the purified bismuth. The integrated flux was determined from the amount of Po\(^{210}\) produced and the 19 millibarns activation cross section for RaE from which the Po\(^{210}\) was derived. This half-life is thus calculated in a very indirect fashion and may be considered an upper limit.

From the information available in 1954 Levy and Perlman\(^{107}\) constructed a decay scheme for the isomers which was consistent with all the then known properties. This decay scheme indicated that the energy difference between the two isomers was only a few kilovolts and that Radium E probably was slightly higher in energy than Bi\(^{210}\) (long). This decay scheme assumed that the observed alpha group of 4.935 MeV energy represented the ground state transition and was crucially dependent on an O- shell model assignment for Radium E. When the spin of Radium E was determined to be 1 by the atomic beam method,\(^{99}\) and when further information was obtained on the alpha particles of both isomers this decay scheme had to be abandoned. We turn now to a discussion of later data on the alpha spectra.

Broda and Feather\(^{94}\) established the existence of a slight branching decay of Radium E by alpha emission. They did this by isolating the daughter product Tl\(^{206}\) and established a branch decay of \((1.2 \text{ to } 10) \times 10^{-7}\). Fink et al.\(^{110}\) confirmed this. Walen and Bastin\(^{111}\) carried this work further and measured the energies of the alpha particle groups. The results of this study are given in Table 6.13.

Golenetskii, Rusinov and Filimonov\(^{112}\) procured a sample of the long-lived isomer with the higher specific activity of 14,000 alpha disintegrations per minute per milligram. With this sample they were able to measure the

---

Table 6.13 Alpha Groups of Radium E

<table>
<thead>
<tr>
<th>$E_\alpha$ (MeV)</th>
<th>Intensity per Disintegration</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.686</td>
<td>$0.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>4.649</td>
<td>$0.75 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Walen and Bastin, J. Phys. et Rad. 20, 589 (1959). On the energy scale used by these authors the Po$^{210}$ alpha particles is 5.305 MeV.
complex spectrum reported in Table 6.14 by an ionization chamber technique. These workers in collaboration with ANDREEV and KISLOV\textsuperscript{112a} studied the gamma ray photons and conversion electrons emitted by the sample. They found photons of $262 \pm 10$, $301 \pm 10$, $340 \pm 15$ and $620 \pm 20$ keV and conversion electrons of $262 \pm 5$ and $301 \pm 5$ keV transitions. Some crucial information for construction of the decay scheme was obtained by alpha-electron and alpha-gamma coincidence experiments.

Particularly important was the finding that the most energetic alpha group was in coincidence with $262$ keV photons. These new results are incorporated into the decay scheme shown here as Figs. 6.18 and 6.19. The half-lives of the Tl\textsuperscript{206} levels at 262 and 301 keV were determined to be $1.2 \times 10^{-9}$ seconds and $3.2 \times 10^{-9}$ seconds, respectively. A small amount of Po\textsuperscript{210} alpha activity, which did not decay with the Po\textsuperscript{210} half-life, was found in the alpha spectrum. This indicates the existence of a slight $\gamma$-decay of Bi\textsuperscript{210m} to form RaE. Based on a $2.6 \times 10^6$ year half-life for Bi\textsuperscript{210m} the partial half-life of the isomeric transition is $\sim 5 \times 10^{10}$ years.

This Russian work clearly establishes that the long-lived isomer of Bi\textsuperscript{210} lies approximately 250 keV above Radium E in mass. A reasonable spin assignment for the isomer is $\frac{9}{2}^-$ based on a $\frac{9}{2}^-$ neutron and an $\frac{9}{2}^+$ proton with spins aligned in the same direction. The large spin difference of 8 then accounts for the long half-life for the isomeric transition.

The level systems of Bi\textsuperscript{210} and of Tl\textsuperscript{206} are quite interesting from the shell model point of view as both nuclides are but one proton and one neutron removed from closed shells. The possible shell model wave functions available to these particles are known from data on neighboring odd-A nuclei and the residual forces between the odd-proton and the odd-neutron can be estimated. NEWBY and KONOPINSKI\textsuperscript{102} have discussed the levels of Bi\textsuperscript{210}. SLIV, SOGOMONOVA and KHARITONOV\textsuperscript{113a} have discussed both Bi\textsuperscript{210} and Tl\textsuperscript{206} from a theoretical standpoint. WALLEN and BASTIN-SCOFFIER\textsuperscript{113} and ZEH and MANG\textsuperscript{114}.

### Table 6.14 Alpha Groups of Bi\textsuperscript{210} (long)

<table>
<thead>
<tr>
<th>Alpha Groups</th>
<th>$E_\alpha$ (MeV)</th>
<th>Relative Intensity</th>
<th>Energy of Excited States (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_0$</td>
<td>not detected</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>$\alpha_{260}$</td>
<td>4.93 ± 0.01</td>
<td>60</td>
<td>262</td>
</tr>
<tr>
<td>$\alpha_{300}$</td>
<td>4.89 ± 0.01</td>
<td>34</td>
<td>300</td>
</tr>
<tr>
<td>$\alpha_{610}$</td>
<td>4.59 ± 0.01</td>
<td>5</td>
<td>610</td>
</tr>
<tr>
<td>$\alpha_{720}$</td>
<td>4.48 ± 0.015</td>
<td>~0.5</td>
<td>720</td>
</tr>
</tbody>
</table>

Golenetskii, Rusinov and Filimanov, Sov. Phys. JETP, 10, 395 (1960) and Rusinov, Andreev, Golenetskii, Kislov and Filimonov, Sov. Phys. JETP 13, 707 (1961). Energies are relative to Th\textsuperscript{230}($E_\alpha = 4.682$ MeV), U\textsuperscript{233}($E_\alpha = 4.816$ MeV), Pu\textsuperscript{239}($E_\alpha = 5.147$ MeV) and Am\textsuperscript{241}($E_\alpha = 5.480$ MeV).
Fig. 6.18. Overall decay scheme of Radium DEF complex and of the Bi$^{210}$ isomers. See also Fig. 6.19.
Fig. 6.19. Detailed decay scheme of Bi$^{210}$ isomers. The shell model assignments give the proton assignment first.
have also discussed the decay schemes of the Bi$^{210}$ isomers in the light of
the shell model.

It would be desirable to have a redetermination of the alpha half-
life of Bi$^{210}$ (long) by a more direct method. To secure agreement with the
expected decay rate estimated from decay rates of nearby nuclei one would
need a half-life of about $5 \times 10^5$ years. ZEH and MANG$^{114}$ have made calculations
of the alpha spectrum of Radium E by a method in which the alpha particle wave
function is projected out of the shell model wave functions of individual
particles. This calculation is a sensitive test of the shell model wave
functions contributing to parent and daughter levels.

Radium G = (Uranium lead). The stable end-product of the uranium
radium decay chain is Pb$^{206}$ known as RaG or uranium-lead. The isotopic
abundance of Pb$^{206}$ compared to the other uranium isotopes had considerable
importance historically in the understanding of natural radioactivity and
continues to have great significance for dating of minerals, etc. These
matters are discussed in Sec. 6.5 of this chapter.
6.3 THE THORIUM (4n) SERIES

The second of the three naturally-occurring series of radioactive elements which we discuss in this chapter is the thorium series. This series originates with Th$^{232}$ which is the primary activity and terminates with the stable nuclide, Pb$^{208}$. The course of the decay chain is shown in Fig. 6.20 and Table 6.15.

The thorium series could be extended indefinitely to elements above thorium as follows:

\[
\begin{align*}
\text{Cm}^{244} & \xrightarrow{\alpha} \text{Pu}^{240} \quad \text{17.9 years} \quad \alpha \quad \text{Pu}^{240} \xrightarrow{\alpha} \text{U}^{236} \quad \text{2.39 x 10}^7 \text{ yr} \quad \alpha \quad \text{Th}^{232}
\end{align*}
\]

It is quite possible that several of these higher members of the series were present at the time the elements were formed, but in the long period which has elapsed since (more than 4.5 billion years) these precursors of thorium have completely decayed to the much longer-lived thorium.

Thorium. BERZELIUS discovered thorium in 1828 in a Norwegian mineral, but the fact that thorium was radioactive was not discovered until the independent experiments of Mme. CURIE and G.C. SCHMIDT in 1898. Before the discovery of nuclear fission, the principal interest in thorium, aside from its radioactive properties, resided in the fact that thorium was a very superior material for the preparation of incandescent gas mantles. This discovery of AUER VON WELSBACH gave rise to a thriving industry until the more efficient electric incandescent lamp industry was well-established. Thereafter, interest in thorium chemistry, minerology and metallurgy declined until the discovery of nuclear fission and the successful release of nuclear energy. Thorium itself does not fission upon capture of slow neutrons, but it can be converted into the fissile nuclide U$^{233}$ by neutron irradiation, as was first demonstrated by SEABORG, GOFMAN and STOURTON.\textsuperscript{115}

Fig. 6.20. The thorium (4n) decay series.
<table>
<thead>
<tr>
<th>Radioelement</th>
<th>Symbol</th>
<th>Radiation</th>
<th>Half-life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thorium</td>
<td>Th$^{232}$</td>
<td>α($\beta^-$ stable)</td>
<td>$1.39 \times 10^{10}$ y</td>
</tr>
<tr>
<td>Mesothorium 1</td>
<td>Ra$^{228}$</td>
<td>β</td>
<td>6.7 y</td>
</tr>
<tr>
<td>Mesothorium 2</td>
<td>Ac$^{228}$</td>
<td>β</td>
<td>6.13 h</td>
</tr>
<tr>
<td>Radoithorium</td>
<td>Th$^{228}$</td>
<td>α($\beta$ stable)</td>
<td>1.91 y</td>
</tr>
<tr>
<td>Thorium X</td>
<td>Ra$^{224}$</td>
<td>α($\beta$ stable)</td>
<td>3.64 d</td>
</tr>
<tr>
<td>Thoron</td>
<td>Em$^{220}$</td>
<td>α($\beta$ stable)</td>
<td>51.5 s</td>
</tr>
<tr>
<td>Thorium A</td>
<td>Po$^{216}$</td>
<td>α($\beta$ stable)</td>
<td>0.158 s</td>
</tr>
<tr>
<td>Thorium B</td>
<td>Pb$^{212}$</td>
<td>β</td>
<td>10.64 h</td>
</tr>
<tr>
<td>Thorium C</td>
<td>Bi$^{212}$</td>
<td>β$^-$ (64%)</td>
<td>60.5 m</td>
</tr>
<tr>
<td>Thorium C'</td>
<td>Po$^{212}$</td>
<td>α($\beta$ stable)</td>
<td>$3.04 \times 10^{-7}$ s</td>
</tr>
<tr>
<td>Thorium C''</td>
<td>Tl$^{208}$</td>
<td>β</td>
<td>3.1 m</td>
</tr>
<tr>
<td>Thorium D</td>
<td>Pb$^{208}$</td>
<td>stable</td>
<td></td>
</tr>
</tbody>
</table>
\[
\text{Th}^{232}(n,\gamma)\text{Th}^{233} \xrightarrow{23.3 \text{ min}} \text{Pa}^{233} \xrightarrow{27.4 \text{ days}} \text{U}^{233}
\]

\[\sigma = 7.5 \text{ barns}\]

This reaction provides a means by which the world's total supply of nuclear fuel can be increased manyfold. To do this it would be necessary to build "breeder" or "converter" reactors in which excess fission neutrons were absorbed in thorium to produce \(\text{U}^{233}\).

Thorium is widely distributed in the earth's crust. It is estimated that the average thorium content of the outermost layer of the earth is 12 parts per million or approximately three times greater than uranium. The most important commercial source of thorium is monazite, which is a rare-earth orthophosphate in which thorium occurs as a minor constituent. Large deposits are found in Brazil, India, Ceylon and Australia. Thorium exists in a great variety of minerals as a minor constituent and only in a very few as a major component; none of these latter have the commercial importance of monazite. The half-life of thorium was reported to be \(1.31 \times 10^{10}\) years by GEIGER and RUTHERFORD\(^{116}\) in the year 1910. This value was based upon the determination of the number of alpha particles emitted per gram of thorium in equilibrium with all its daughters and the knowledge that 6 alpha particles were emitted during the total transformation sequence. This early half-life determination is very close to the redeterminations cited in Table 6.16 carried out at a much later date. In this book we accept the value of \(1.39 \times 10^{10}\) found by KOVARIK and ADAMS in 1938. The total specific alpha activity of pure thorium may vary considerably depending upon the amount of radiothorium present in the sample; this in turn depends upon the history of the sample. The reasons for this may be visualized by consulting Fig. 6.20.

When thorium is purified the equilibrium amount of radiothorium will remain with the thorium since radiothorium is an isotope of thorium. In a matter of days (See Fig. 6.26 below) the remainder of the series below radiothorium will grow back into equilibrium with the radiothorium. The total alpha

Table 6.16 Determinations of the Half-Life of Thorium

<table>
<thead>
<tr>
<th>Researcher</th>
<th>Journal</th>
<th>Year</th>
<th>Half-Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kovarik and Adams</td>
<td>Phys. Rev.</td>
<td>1938</td>
<td>$1.39 \times 10^{10}$ years</td>
</tr>
<tr>
<td>Picciotto and Wilgain</td>
<td>Nuovo Cim.</td>
<td>1956</td>
<td>$1.39 \times 10^{10}$ years $\pm 2$</td>
</tr>
<tr>
<td>Macklin and Pomerance</td>
<td>J. Nuclear Energy</td>
<td>1956</td>
<td>$1.45 \times 10^{10}$ years</td>
</tr>
<tr>
<td>Senftle, Farley and Lazar</td>
<td>Phys. Rev.</td>
<td>1956</td>
<td>$1.42 \times 10^{10}$ years $\pm 5$</td>
</tr>
<tr>
<td>T.A. Farley</td>
<td>Can. J. Phys.</td>
<td>1960</td>
<td>$1.41 \times 10^{10}$ years $\pm 1%$</td>
</tr>
</tbody>
</table>

Adopted "best" value: $1.39 \times 10^{10}$ years

Decay Constant $\lambda =$ $4.98 \times 10^{-9}$ years$^{-1}$
Specific activity = $246$ dis/min$^{-1}$ mg$^{-1}$

* This value was determined by determining an absolute gamma-disintegration rate for Tl$^{208}$ (Ra"C") in equilibrium with aged thorium salts.
activity will then be six times the activity of $\text{Th}^{232}$ alone. However, the radiothorium and its decay products will begin to decay with the 1.9 year half-life of radiothorium because the 6.7 year radium isotope, mesothorium-1, was removed during the chemical purification. Over a period of years the mesothorium will grow back into the thorium provided the thorium is not subjected to further chemical purification. The net result is that the amount of radiothorium and the total alpha activity declines to a minimum at 5 years and then slowly rises again until complete equilibrium with $\text{Th}^{232}$ is once more established. These specific activity changes in thorium are quite appreciable over normal periods of storage and use in commerce or in the laboratory. In this respect pure thorium is quite unlike pure natural uranium which would have to be stored for 2000 years before the specific alpha activity increased by as much as one percent. The specific activity changes in thorium are shown quantitatively in Fig. 6.21. Another effect which can contribute to the specific alpha activity of thorium is ionium contamination. If thorium is isolated from an ore containing appreciable amounts of uranium, the ionium will add appreciably to the specific activity even though the contamination on an atom basis is miniscule.

The long half-life of thorium makes it somewhat difficult to measure the specific activity or to measure the alpha particle energy because of self-absorption effects. Some careful measurements in a gridded ionization chamber have shown the alpha particle energy of the main alpha particle group to be 4.007 MeV. However, a smaller peak appears in the pulse spectrum from the ion chamber corresponding to an alpha particle group of about 55 keV less energy. Several investigators have confirmed the presence of this lower energy group by impregnating nuclear emulsions with thorium salts and observing electron tracks from the conversion of a 55-60 keV gamma transition emanating from the same point as many of the alpha tracks. The

---

Fig. 6.21. Change in amount of radiothorium (Th$^{228}$) and change in the total alpha activity to be found in Th$^{232}$ starting with pure thorium freshly isolated from an undisturbed ore sample. The decay of RdTh initially present and the regrowth of RdTh into the sample via the decay sequence below are shown separately:

\[
\begin{align*}
\text{Th}^{232} \xrightarrow[1.39 \times 10^{10} \text{ yrs.}]{\alpha} \text{MsTh}_1 \xrightarrow[6.7 \text{ yrs}]{\beta^-} \text{MsTh}_2 \xrightarrow[6.13 \text{ hrs.}]{\beta^-} \text{RdTh} \xrightarrow[1.90 \text{ yrs.}]{\alpha}
\end{align*}
\]

The uppermost curve is the total specific alpha activity of the thorium; this consists of a constant activity = 1 contributed by Th$^{232}$ and the variable contribution of RdTh plus the 4 short lived alpha-emitting descendants of RdTh. The relative value 1 on the ordinate scale is equivalent on an absolute scale to 246 disintegrations per minute for one milligram of thorium.
intensities of the main alpha particle group and the lower energy group are 76 percent and 24 percent, respectively. A third alpha group has been observed in 0.2 percent intensity at an energy 185 keV below the main group. It is likely that other alpha particle groups and gamma rays are present in the decay of thorium but in very low abundance.

Normal thorium is essentially monoisotopic on an atom percent basis because the only other thorium isotope in the decay series, RdTh, is present only to the extent of 5 parts in 10^10. This made it possible to determine the atomic mass number of thorium rather early in the history of radioactivity. This was important as it made it possible to assign correct mass numbers to all radioelements which could be related to thorium by a series of α and β transformations. Very precise measurements of the atomic weight of thorium were published by Honigschmid in 1916, his preferred value being 232.12. Since that time the mass spectrometric method has replaced chemical weighing methods for atomic weight determination. Stanford, Duckworth, Hogg and Geiger in 1952 reported a value of 232.1093 ± 0.0010 atomic mass units. Other redeterminations are listed in Table 2.4 in Chapter 2.

Thorium in equilibrium with all its radioactive descendents contains on a weight basis, the very small amounts of the products listed in Table 6.17.

Mesothorium 1 (Ra and Mesothorium 2 (Ac). The immediate product of Th decay is the 6.7 year beta-emitter MsTh, an isotope of radium. Since the total decay energy is only 55 keV the radiations of MsTh are extremely weak and are difficult to detect and measure accurately because of self absorption and window absorption effects. Literature reports on its radiations are not in complete agreement. Among recent reports, careful study by Goetze revealed a single ground-state-to-ground-state beta transition with 55 ± 3 keV energy (log ft = 5.6). He found no conversion electrons, x-rays or gamma ray photons. On the other hand Tousset saw low energy electrons interpreted as the conversion electrons of a 10.5 keV transition.

---

Table 6.17 Amount of Individual Thorium Decay Products in Ore Relative to the Amount of Thorium

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-life</th>
<th>Relative Amount by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th$^{232}$</td>
<td>$1.39 \times 10^{10}$ y</td>
<td>1.0</td>
</tr>
<tr>
<td>Ra$^{228}$ ($\alpha$Th$_1$)</td>
<td>6.7 y</td>
<td>$4.74 \times 10^{-10}$</td>
</tr>
<tr>
<td>Th$^{228}$ ($\beta$Th)</td>
<td>1.91 y</td>
<td>$1.34 \times 10^{-10}$</td>
</tr>
<tr>
<td>Ra$^{224}$ ($\beta$X)</td>
<td>3.64 d</td>
<td>$7 \times 10^{-13}$</td>
</tr>
</tbody>
</table>
occurring in 25 percent of the disintegrations. One of the great difficulties in a study of this nuclide is that after MsTh$_1$ is purified, daughter activity of the 6.13 hour MsTh$_2$, an isotope of actinium, quickly grows in. This isotope has a total beta decay energy of 2.18 MeV and decays with the emission of a complex mixture of electrons and gamma rays. Six groups of beta rays have been identified ranging in energy from 450 keV to 2.18 MeV. A number of gamma rays ranging in energy from 58 keV to 1640 keV have been reported. The radiations of MsTh$_2$ are discussed in some detail in the next subsection.

The combination of MsTh$_1$ and MsTh$_2$ is a favorable one for many medical or industrial uses involving a need for an intense source of high energy gamma radiation since the MsTh$_1$ gives the combination a conveniently long half-life. For some years mesothorium sources were sold in competition with Ra$^{226}$ sources. In recent years mesothorium has been replaced in many instances by radioactive isotopes prepared in nuclear reactors.

The gamma activity of a mesothorium sample does not decay with a simple 6.7 year half-life because of the growth of radiothorium (plus its short-lived daughters) into the mesothorium. This growth is shown quantitatively in Fig. 6.23. Some of the shorter-lived descendents of radiothorium, particularly ThC, have hard gamma radiation. Hence a mesothorium preparation will have variable total hard gamma radiation rising to a maximum in about five years.

Mesothorium isolated from thorium which is both chemically and isotopically pure will be pure on both an atom basis and an activity basis (after allowing a few weeks for decay of ThX). The amounts which can be prepared is somewhat limited as can be seen from Fig. 6.22. Larger amounts are readily prepared by isolating a radium fraction from thorium ores. Such samples contain a variable amount of Ra$^{226}$ depending on the ratio of thorium to uranium in the ore. Similarly Ra$^{226}$ samples isolated from uranium ores may contain some mesothorium contamination because of thorium present in the uranium ore. A convenient way to analyze for the amounts of these two radium isotopes in an aged radium preparation is to remove the gaseous emanation fraction and to measure the amount of 54.5 second thoron and 3.825 day radon.

Mesothorium is used in the preparation of photoneutron sources. (See Sec. 5.5.4 and Table 5.21 in Chapter 5). The usefulness of mesothorium depends
Fig. 6.22. Growth of MsTh₁ (6.7 y Ra²²⁸) into pure Th²³₂.
Fig. 6.23. Growth of radiothorium (1.9 y Th$_{228}$) into pure MsTh$_1$ (6.7 y Ra$_{228}$). Since the half-lives of all the radioactive descendents of RaTh are short-lived compared to RaTh this curve can be taken to represent the growth of all these products into pure MsTh$_1$. 
upon the growth of ThC and ThC", which have high energy high intensity gamma rays. The 2.62 MeV gamma ray in the decay of ThC" is particularly effective.

The Radiations of MβTh₂ (Ac²²⁸). Several sets of measurements of the numerous conversion electrons and photons emitted in the decay of mesothorium-2 are summarized in the accompanying tables. The most comprehensive study is that of BJÖRHOLM, NATHAN, NIELSEN and SHELINE from which we chiefly quote here in discussing the decay scheme. The precise values for transition energies and the multipolarity assignments of the most prominent gamma rays form the most important basis for the construction of a decay scheme, but very important contributory evidence comes from coincidence experiments of the electron-electron, electron-gamma, beta-gamma, and gamma-gamma types.

The daughter product is the even-even nucleus Th²²⁸. The observed levels of excitation resemble those known to occur systematically throughout the heavy element group of nuclides; namely levels of collective rotation and vibration of a deformed nucleus. Thorium 228 is also the product of the alpha decay of U²³² and the electron capture decay of Pa²²⁸, both of which have been thoroughly studied, so that many features of the level schemes of Th²²⁸ are firmly fixed by a consideration of three independent decay schemes. The most extensive information comes from a study of the electron capture decay of Pa²³². Consequently a more comprehensive discussion of the Th²²⁸ level scheme is given in Chapter 8 where the decay of Pa²²⁸ is discussed (Sec. 8.3.4).

The low-lying levels of Th²²⁸ seen in the decay of Ac²²⁸ are shown in Fig. 6.24. The 0+, 2+, 4+ levels at 0, 58 and 157 keV, respectively,

Table 6.18 Gamma Transitions of Ac$^{228}$

<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>Black$^{124}$</th>
<th>Thibaud$^{125}$</th>
<th>Kyles, Campbell and Henderson$^{126}$</th>
<th>Brodie$^{127}$</th>
<th>Box and Klaiber$^{128}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>58</td>
<td>--</td>
<td>56.75</td>
<td>57.0</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>--</td>
<td>78.05</td>
<td>78.1</td>
<td>--</td>
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</tr>
<tr>
<td>--</td>
<td>--</td>
<td>97.77</td>
<td>97.4</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>113.0</td>
<td>--</td>
<td>--</td>
<td></td>
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<tr>
<td>129</td>
<td>--</td>
<td>127.5</td>
<td>127.5</td>
<td>127</td>
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</tr>
<tr>
<td>--</td>
<td>--</td>
<td>179.0</td>
<td>--</td>
<td>155</td>
<td></td>
</tr>
<tr>
<td>184</td>
<td>--</td>
<td>184.2</td>
<td>183.7</td>
<td>--</td>
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<td>--</td>
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<td>--</td>
<td>--</td>
<td>220</td>
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</tr>
<tr>
<td>250</td>
<td>--</td>
<td>232.2</td>
<td>--</td>
<td>278</td>
<td></td>
</tr>
<tr>
<td>338</td>
<td>333</td>
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<td>--</td>
<td>336</td>
<td></td>
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<td>--</td>
<td>--</td>
<td>410.1</td>
<td>--</td>
<td>410</td>
<td></td>
</tr>
<tr>
<td>462</td>
<td>462.</td>
<td>457.6</td>
<td>--</td>
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<tr>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>790</td>
<td></td>
</tr>
<tr>
<td>914</td>
<td>913</td>
<td>907.1</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>969</td>
<td>968</td>
<td>964.5</td>
<td>--</td>
<td>935 (complex)</td>
<td></td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>1035</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>1095</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>1587</td>
<td>--</td>
<td>1587</td>
<td></td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>1640</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>
Table 6.19 Gamma Transitions of $^{228}$Ac Conversion Electron Studies of Bjørnholm and co-workers.\textsuperscript{129,130}

<table>
<thead>
<tr>
<th>$E_\gamma$ (keV)</th>
<th>Transition Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>57.5</td>
<td>70</td>
</tr>
<tr>
<td>99.4</td>
<td></td>
</tr>
<tr>
<td>129.1</td>
<td>10.5</td>
</tr>
<tr>
<td>137.8</td>
<td></td>
</tr>
<tr>
<td>178.0</td>
<td></td>
</tr>
<tr>
<td>184.5</td>
<td></td>
</tr>
<tr>
<td>209.0</td>
<td>4</td>
</tr>
<tr>
<td>270.0</td>
<td>3.1</td>
</tr>
<tr>
<td>282.2</td>
<td></td>
</tr>
<tr>
<td>327.5</td>
<td>3.3</td>
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<tr>
<td>338.5</td>
<td>9.5</td>
</tr>
<tr>
<td>409.7</td>
<td></td>
</tr>
<tr>
<td>443</td>
<td></td>
</tr>
<tr>
<td>463.3</td>
<td></td>
</tr>
<tr>
<td>473</td>
<td></td>
</tr>
<tr>
<td>484</td>
<td></td>
</tr>
<tr>
<td>510</td>
<td></td>
</tr>
<tr>
<td>555</td>
<td></td>
</tr>
<tr>
<td>573</td>
<td></td>
</tr>
<tr>
<td>619</td>
<td></td>
</tr>
<tr>
<td>749</td>
<td></td>
</tr>
<tr>
<td>756.2</td>
<td></td>
</tr>
<tr>
<td>769</td>
<td></td>
</tr>
<tr>
<td>773.5</td>
<td>(0.8)</td>
</tr>
<tr>
<td>782.6</td>
<td></td>
</tr>
<tr>
<td>795.8</td>
<td>(4.5)</td>
</tr>
<tr>
<td>836.4</td>
<td>(1.6)</td>
</tr>
<tr>
<td>912.2</td>
<td>25</td>
</tr>
<tr>
<td>924</td>
<td></td>
</tr>
<tr>
<td>970.0</td>
<td></td>
</tr>
<tr>
<td>966.0</td>
<td>19</td>
</tr>
<tr>
<td>1464</td>
<td></td>
</tr>
<tr>
<td>1593</td>
<td></td>
</tr>
</tbody>
</table>

Energies from Arbman, Bjørnholm and Nielsen.\textsuperscript{130} Intensities from Bjørnholm, Nathan, Nielsen and Sheline.\textsuperscript{129}
constitute the familiar rotational band of levels for an axially-symmetric but non-spherical nuclear ground state. The 58 keV transition is thoroughly characterized as E2 by its L-subshell conversion ratios. This transition is almost completely converted ($\alpha_L = 144\%$) so that no photons are observed. The lifetime of the 58 keV level was found to be $(4.0 \pm 0.3) \times 10^{-10}$ seconds. The corresponding E2 transition probability is more than 200 times the single particle transition value which confirms the collective nature of the state. The 127.5 keV transition connecting the $4^+$ and $2^+$ levels is also an electric quadrupole transition as deduced from the K/L conversion ratio and the prominent conversion in the $L_\text{II}$ and $L_\text{III}$ subshells. These two radiations are also prominent in the alpha decay of U$^{232}$.

A prominent 184-keV transition seen in the decay of Ac$^{228}$ has the K/L ratio and the high $L_\text{I}/L_\text{II} + L_\text{III}$ subshell conversion ratio expected of an M1 transition. Kyles and co-workers$^{126}$ and Box and Klaiber$^{128}$ regarded this gamma ray as a crossover transition from a 184-keV $1^+$ level in parallel with a 127.5-57 keV cascade. In view of the spin assignments and the rotational band interpretation of the low-lying levels given here and in view of the non-observance of this gamma ray in U$^{232}$ alpha decay$^{133}$ this postulate is untenable. Bjørnholm and co-workers$^{129}$ found that the 184-keV transition is coincident with gamma rays de-exciting a level at 966 keV and interpret it as a transition connecting levels at 1050 and 966 keV.

Bjørnholm, Nathan, Nielsen and Seline$^{129}$ found an endpoint energy of 2100 keV for the most energetic beta group and further found that this beta group was strongly coincident with low energy electrons but with no gamma rays. It is thus confirmed that this beta group excites the 58 keV level. The beta intensity is 12%.

* In earlier literature reports surprisingly long half-lives of $\gtrsim 0.01$ seconds$^{126,131}$ and $\gtrsim 0.5$ seconds$^{132}$ were reported for this transition. These reports were not confirmed by later studies$^{133,134}$ made specifically to check then, nor by the study quoted here.$^{129}$

In Fig. 6.24 occur a pair of levels at 328 keV and 396 keV which are given assignments of 1- and 3-, respectively. This pair of levels is interpreted as the beginning of a rotational band based on a 1- state which represents the excitation of an octupole (pear-shaped) deformation of the nucleus. Collective levels of this type are seen systematically in the heavy element group of nuclides. The pattern of gamma ray de-excitation seen in the Th$^{228}$ is similar to that observed before and predicted by theory. The 1- level de-excites by a pair of El transitions to the 0+ and 2+ members of the ground state rotational band. The 3- level de-excites by a pair of El transitions to the 2+ and 4+ members of that band. According to theory the relative transition probabilities of the γ-transitions in these two pairs of El transitions after the energy dependence has been factored out (i.e., the ratios of the reduced transition probabilities) should be given by Clebsch-Gordon coefficient ratios. The observed ratios in the two cases are in agreement with theory for the K and I quantum number assignments given to the levels in Fig. 6.24.

Above the negative parity rotational band there is a gap until a pair of levels at 966 and 1018 keV is reached. The 966 keV level is de-excited by electric quadrupole transitions to the 0+ and 2+ levels of the ground state rotational band. This fixes the spin of the 966 keV level as 2+. It is suggested that this level represents the first quantum state of a quadrupole vibration around the equilibrium spheroidal shape of the nucleus. Further, this vibrational excitation is believed to be of the γ-vibrational type discussed in Chapter 3. The quantum numbers K, I and  are 2, 2 and 1, respectively. The level at 1018 has the spacing above the 966 keV level and the gamma ray de-excitation pattern expected for the first (3+) rotational level based on the 2+ vibrational state. Its position is also well-established by coincidence experiments.

A number of other higher-lying levels have been identified as shown in Fig. 6.25. The existence of these levels is confirmed by the study of the orbital electron decay of Pa$^{228}$. In addition, a number of other levels are observed by the study of the Pa$^{228}$ radiations which may also occur in the beta decay of Ac$^{228}$. Further remarks concerning the interpretation of these upper levels is made in Sec. 8.3.4 of Chapter 8. Figure 6.25 does not
Fig. 6. Low-lying levels of Th$^{228}$ seen in the decay of Ac$^{228}$. From Bjørnholm et al. The numbers associated with the vertical arrows are transition intensities.
Fig. 6.25. Decay scheme of Ac$^{228}$ (MsTh$_2$) as formulated by Bjørnholm, Nathan, Nielsen. Compare with decay scheme of Pa$^{228}$ which appears in Section 8.3.4. The numbers associated with the vertical arrows are transition intensities.
include many of the lower intensity gamma transitions listed in the tables.

The continuous beta spectrum of Ac$^{228}$ was resolved into the six groups shown in Table 6.20 by KYLES, CAMPBELL and HENDERSON. It was suggested by them that the most energetic component excites the 58 keV level in Th$^{228}$. This was confirmed by BJÖRNHOLM ET AL. who found a strong coincidence of the most energetic beta particles with low energy electrons but with no γ-rays. These authors deduced the values of beta group intensities and log ft values summarized in Table 6.20 (b), basing their calculations chiefly on gamma transition intensity balances.

The levels most heavily populated by the beta decay of Ac$^{228}$ have spin 2 and 3 which suggests a spin value $I = K = 2$ or 3 for Ac$^{228}$ with 3 the more probable. The low intensity for the β-decay to the two lowest rotational bands relative to the transitions to high energy levels is thus probably caused by K-forbiddeness. This effect may also explain the fact that an excited β-vibrational band with $K = 0$ and $I = 0^+, 2^+, 4^+ \ldots$ has not been observed. The $I = 0^+$ level of such a band might be expected at about 650 keV in Th$^{228}$.

Radiothorium (Th$^{228}$). We have already seen in Figs. 6.21 and 6.23 how the amount of the alpha-emitter, radiothorium, varies with time in an initially pure sample of thorium or mesothorium. It is clear that a pure sample of radiothorium cannot be isolated directly from thorium ores since at equilibrium, when the RadiumTh/Th$^{232}$ activity ratio is unity, the atom ratio is only $1.4 \times 10^{-10}$. Small samples of isotopically pure RadiumTh can be isolated from mesothorium samples after a few years storage.

A process similar to this sometimes occurs in nature. Water-leaching of a thorium ore may cause the selective removal of the more soluble radium isotope MsTh$^1$ to some location removed from the thorium ore and the subsequent formation of the radiothorium in the new location. Hence it is possible to isolate from nature small samples of radiothorium with a smaller Th$^{232}$ dilution than that corresponding to the equilibrium value.

Radiothorium can be made artificially by irradiating radium or actinium in a high flux reactor, as has been discussed by KIRBY, GROVE and TIMMA. $^{136}$

Table 6.20 Beta Groups of Ac\textsuperscript{228} (MsTh\textsubscript{2})\textsuperscript{126}

Kyles, Campbell and Henderson

<table>
<thead>
<tr>
<th>Energy (MeV)</th>
<th>Abundance %</th>
<th>Log ft.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.18</td>
<td>10.1</td>
<td>8.9</td>
</tr>
<tr>
<td>1.85</td>
<td>9.6</td>
<td>8.7</td>
</tr>
<tr>
<td>1.70</td>
<td>6.7</td>
<td>8.6</td>
</tr>
<tr>
<td>1.11</td>
<td>53.0</td>
<td>7.1</td>
</tr>
<tr>
<td>0.64</td>
<td>7.6</td>
<td>7.2</td>
</tr>
<tr>
<td>0.45</td>
<td>13.0</td>
<td>6.4</td>
</tr>
</tbody>
</table>
Table 6.20 (b) Beta Groups of Ac\textsuperscript{228} (MsTh\textsubscript{2})

Björnholm and co-workers.\textsuperscript{129,130}

<table>
<thead>
<tr>
<th>Energy of Daughter level (keV)</th>
<th>K,I,\pi for level</th>
<th>(\beta)-intensity</th>
<th>log ft.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0,0,\text{+}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>57.5*</td>
<td>0,2 \text{+}</td>
<td>12</td>
<td>8.8</td>
</tr>
<tr>
<td>327.5</td>
<td>0,1\text{-}</td>
<td></td>
<td>9.5</td>
</tr>
<tr>
<td>395.8</td>
<td>0,3\text{-}</td>
<td>12</td>
<td>8.5</td>
</tr>
<tr>
<td>969.5</td>
<td>2,2 \text{+}</td>
<td>35</td>
<td>7.3</td>
</tr>
<tr>
<td>1023.2</td>
<td>2,3 \text{+}</td>
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<td>8.0</td>
</tr>
<tr>
<td>1123.4</td>
<td>2,2 \text{-}</td>
<td>6</td>
<td>8.0</td>
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<td>1154.0</td>
<td>3,3 \text{+}</td>
<td>7</td>
<td>7.7</td>
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<tr>
<td>1432.8</td>
<td>7,4 \text{+}</td>
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<td>8.0</td>
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<td>1451.0</td>
<td>7,3 \text{+}</td>
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<td>1532.2</td>
<td>7,4 \text{+}</td>
<td>6</td>
<td>7.1</td>
</tr>
<tr>
<td>1650.0</td>
<td>2,3 \text{+}</td>
<td>4</td>
<td>6.8</td>
</tr>
</tbody>
</table>

*The energy of the beta group populating this level was reported as 2100 keV.
The radiothorium isolated from neutron-irradiated radium or actinium is contaminated with 18 day Th\textsuperscript{227} (Radioactinium) which comes from the beta decay of Ac\textsuperscript{227}. The amount of this contamination depends on the integrated flux and on the time elapsed since the actinium-thorium separation was made.

Radiothorium may also be isolated as the decay product of U\textsuperscript{232}. If the U\textsuperscript{232} is mixed with U\textsuperscript{233} there will be some contamination with the 7340 year Th\textsuperscript{229} daughter product of U\textsuperscript{233}.

The alpha spectrum of radiothorium has been investigated by ASARO, STEPHENS and PERLMAN\textsuperscript{137} who reported the following groups:

- 5.421 MeV   71 percent
- 5.338 MeV   28 percent
- 5.208 MeV   0.4 percent
- 5.173 MeV   0.2 percent
- 5.137 MeV   0.03 percent

All energies relative to $E_{\alpha}^{Ra\textsuperscript{224}} = 5.681$ MeV.

The alpha particles reveal excited states at 84 keV (2+), 253 keV (4+), at 217 keV (1-) and at 289 (3-); these levels are de-excited by gamma rays of 84 keV, 169 keV, 137 keV and 212 keV. Further details on the characterization of these radiations and on the construction and interpretation of the decay scheme of the Th\textsuperscript{228} are given in Sec. 8.2.6 of Chapter 8.

L. MEITNER\textsuperscript{138} reported the half-life value of 1.907 years in 1918 with an uncertainty of one percent. KIRBY, GROVE and TIMMA\textsuperscript{136} found 1.910 ± 0.002 years in their 1955 redetermination.

Thorium X (Ra\textsuperscript{224}). Pure samples of 3.64 day ThX may be isolated from thorium. To do this, it is necessary first to separate the thorium cleanly from MsTh, and then allow a period of two weeks for the ThX to grow into the

\textsuperscript{138} L. Meitner, Physik. Z. \textbf{19}, 257 (1918).
sample from the radiothorium remaining with the thorium. A radium fraction which is then removed from the thorium consists of pure thorium X. Alternatively, one may isolate ThX from a pure sample of RdTh after a suitable growth period. The growth of ThX into pure RdTh is shown in Fig. 6.26.

Thorium X is an alpha emitter with two prominent alpha particle groups. ROSENBLUM and CO-WORKERS\(^1\) report a main group with energy 5.681 MeV in 95 percent abundance and a second group at 5.448 MeV in 4.6 percent abundance. ASARO, STEPHENS and PERLMAN\(^2\) obtained closely-similar values (5.681 MeV, 95 percent and 5.445 MeV, 4.9 percent). They were unable to detect (upper limit 0.1 percent) a third group at 5.194 MeV which ROSENBLUM\(^1\) had reported to be in 0.4 percent abundance. WALEN and BASTIN\(^3\) restandardized the energy of the main group at the slightly higher value of 5.686 MeV. Gamma ray studies and gamma-gamma coincidence measurements of STEPHENS, ASARO and PERLMAN\(^4\) indicate that 5.15 MeV and 5.04 MeV alpha groups must be present in about 0.009 and 0.012 percent abundance, respectively. WALEN and BASTIN-SCOFFIER\(^5\) confirmed these alpha groups in a careful redetermination of the spectrum; their results include the following groups: 5.684 MeV (94 percent), 5.447 MeV (5.5 percent), 5.159 MeV \(\left(7.3 \times 10^{-3}\right)\) percent), 5.049 MeV \(\left(7.2 \times 10^{-3}\right)\) percent), and 5.032 MeV \(\left(3.1 \times 10^{-3}\right)\) percent).

The decay scheme of Ra\(^{224}\) is shown in Fig. 6.27. The most prominent gamma radiation is the 241.1 keV transition which ROSENBLUM, VALADARES and GUILLOT\(^6\) have characterized in detail. The photon intensity is 3.7 percent, the K conversion coefficient is 0.13 and the K/L\(\text{II}/L\text{III}\) conversion ratio is 0.46/0.3/0.28. The multipolarity of the radiation is electric quadrupole (E2).

MULLER and CO-WORKERS\(^7\) used a crystal spectrometer to determine a very

---

Fig. 6.26. Growth of 3.64 day ThX (Ra$^{224}$) from RdTh (Th$^{228}$).
precise value of 240.98 keV for the energy of the photon. Stephens, Asaro and Perlman\cite{141} used a scintillation spectrometer to find additional gamma rays with the following energies and abundances: 290 keV ($\sim 8 \times 10^{-3}\%$), 410 keV ($\sim 4 \times 10^{-3}\%$), 650 keV ($\sim 9 \times 10^{-3}\%$). The 241 keV gamma ray was observed to be in coincidence with the 290 and 410 keV transitions. These authors have interpreted the level scheme of Fig. 6.27 in the following way. The thoron nucleus is below the mass region where nuclei are stabilized in a non-spherical shape (see Chapter 3), but it lies well beyond the closed shell region and among a group of nuclei which can be deformed rather easily from the spherical ground state. The excited states in Fig. 6.27 are not single particle quantum states representing different intrinsic particle excitation; rather they are quantum states arising from collective motions. The levels at 241 and at 530 keV respectively are simple collective vibrations about the spherical equilibrium state. The absence of a crossover gamma ray from the 530 keV (2+) level to the ground state is strong evidence for this interpretation. (See Sec. 3.3 of Chapter 3.) The level at 650 keV is de-excited by E1 transitions to the ground state and to the first 2+ state. This identifies the 650 keV level as a 1-state. Negative parity states in heavy element even-even nuclei are believed to be the result of collective octupole vibrational motions. This phenomenon is discussed in Chapter 3 (see Sections 3.4.4 and 3.5.3).

Thoron ($^{220}\text{Em}$) and ThA ($^{216}\text{Po}$). Thoron has a half-life of 54.4 seconds and hence comes to equilibrium with its parent, thorium X, within a few minutes. Thorium A, the daughter of thoron, has a half-life of only 0.158 seconds so that ThA alpha activity and thoron alpha activity are virtually inseparable. Thoron emits alpha particles of 6.296 MeV ($\sim 100\%$ abundance) and 5.761 ($\sim 0.3\%$ abundance) and ThA emits alpha particles with an energy of 6.777 MeV;\textsuperscript{143a} ThA emits a small-intensity group of 5.984 MeV particles in $2.1 \times 10^{-3}$ percent intensity.\textsuperscript{143a} A gamma ray of 542 keV energy appears in $\sim 0.03$ percent abundance in thoron decay, corresponding to the difference in energy of the alpha particle groups.

Analysis for thoron is a very sensitive test for the presence of any of the members of the thorium series which lie above it in the decay sequence. The substance to be analyzed can be put into solution and the thoron removed by bubbling a carrier gas through the solution and into an ionization chamber
Fig. 6.27. Decay scheme of Thorium X (Ra$^{224}$). The alpha data are taken from Bastin-Scoffier and Walen.\textsuperscript{143a}
or electrometer. The energetic alpha particles of thoron and ThA are readily detected and a half-life determination identifies the activity conclusively.

For special studies it is possible to collect ThA activity by the recoil collection method on a rapidly-revolving electrically-charged disc. MOSELY and FAJANS (1911) introduced this method of separation of ThA from thoron and used it to determine the half-life of ThA. Their value was 0.14 seconds. A more-precise value of 0.158 seconds was measured in 1942 by A.G. WARD.

A word should be said concerning the beta branching of ThA which has been reported by KARLIK and BERNERT. These workers observed 7.57 MeV alpha particles in a fresh sample of thoron decaying with the 54 second half-life of thoron and ascribed them to At216 arising from a 1.35 x 10^-2 percent beta branching of ThA. Because of the short half-life of ThA there was no chance to observe the growth of these new alpha particles into the fresh thoron sample. This interpretation is open to serious question upon energetic grounds as was recognized by the authors themselves, by FEATHER, by FLÜGGE and KREBS, and by PERLMAN ET AL. and will here be considered untenable. The difficulty is readily understood when the following closed decay-energy cycle is considered.

![Decay Energy Cycle](attachment:image.png)

The total decay energy of ThA and ThB are known from experimental measurements. The decay energy of At216 is known from measurements of At216 present in the

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145. N. Feather, Nucleonics 5, 22 (1949).
decay chain of the artificially-produced isotope, \( \text{Pa}^{228} \). Since the energy changes around the closed cycle must sum to zero, \( \text{At}^{216} \) is actually unstable with respect to ThA by 0.45 MeV and \( \beta^- \) decay of ThA is impossible. For beta decay of ThA to proceed to the extent reported it would be necessary for ThA to be unstable with respect to \( \text{At}^{216} \) by >1.0 MeV.

KARLIK and BERNERT suggested an explanation which retained their assignment of the 7.57 MeV alpha groups to \( \text{At}^{216} \) by assuming that ThB decays only to a 1.15 MeV excited state of \( \text{Bi}^{212} \), this excited state having the properties associated with ThC, while the alpha-decay of \( \text{At}^{216} \) proceeds to the ground state. This explanation seems untenable for a number of reasons. If ThC represents the postulated excited state of \( \text{Bi}^{212} \) then the alpha decay energy from the ground state of \( \text{Bi}^{212} \) would be 1.15 MeV lower than the measured value of ThC (6.2 MeV), that is, about 5.0 MeV. But from the regularities of alpha decay energies we know that the ground state alpha decay energy of \( \text{Bi}^{212} \) must fall between the values for \( \text{Bi}^{211} \) and \( \text{Bi}^{213} \). The value 6.2 MeV fits this requirement whereas 5.0 MeV is completely out of line. In addition, the explanation is in conflict with the known properties of the collateral decay series starting with 22 hour \( \text{Pa}^{228} \) because in this series \( \text{At}^{216} \), arising from the alpha decay of \( \text{Fr}^{220} \), decays to \( \text{Bi}^{212} \) identical in properties with ThC. (See discussion of \( \text{Pa}^{228} \) series in Chapter 7.) All in all, it appears to be highly unlikely that ThA is \( \beta^- \) unstable and therefore the 7.57 MeV low-intensity alpha groups found by KARLIK and BERNERT must arise from some isotope other than \( \text{At}^{216} \). Confirmatory evidence for this point of view comes from the work of BASTIN-SCOFFIER and WALLEN who reinvestigated the alpha spectrum of ThA and found no alpha particles in the energy range 6.800 - 8.600 MeV above an intensity limit of 5 x \( 10^{-4} \) percent.

The Thorium Active Deposit - General Comments. The active deposit left upon the decay of thoron consists of Thorium B,C,C' and C". Thorium A decays so rapidly that in no practical sense is it useful to regard it as a real member of the thorium active deposit even though it is the direct descendant of thoron. Samples of Thorium B can be collected by letting a sample of thoron decay in a capillary tube or in some suitable vessel. All surfaces exposed to the gas will be coated with an invisible deposit of ThB. Alternatively, the non-gaseous products of thoron decay can be collected on a charged wire or metal surface. The electrical collection method makes it possible to
localize the active deposit, which is important in the preparation of beta ray spectrometer sources.

The initial activity of the active deposit consists of nearly-pure 10.6 hour ThB because the growth of the remainder of the decay chain is slowed down by the comparatively long half-life of the 60.5 minute ThC. Pure samples of thorium B can also be isolated chemically from a solution of the active deposit or from a solution of ThX or of radiothorium. The growth of ThB into radiothorium is very nearly the same (on an activity basis) as the growth of ThX shown in Fig. 6.26. The growth of ThB and ThC into ThX is shown by Fig. 6.28. The growth of ThC into ThB is shown in Fig. 6.29.

The electron spectrum of ThB in equilibrium with ThC' and ThC'' is characterized by a large number of conversion electrons. Since the energies of many of these conversion electrons have been very carefully measured, Th(B-C-C'') sources are valuable for calibration of electron spectrometers. An excellent detailed summary of these electrons and examples of the spectrum observed on high resolution permanent magnet spectrographs and semi-circular beta spectrometer are given by K. Siegbahn and T.R. Gerholm.\footnote{148} Energies of some of the principal lines are summarized in Table 6.21.

An overall view of the complex nature of the thorium B active deposit can be obtained from Fig. 6.30. Note the complexity of the $\beta^-$ decay of ThB, ThC and ThC''; note the long-range alpha particles originating from the excited levels of ThC'; note the prominent gamma ray with the very high energy of 2.62 MeV which occurs in 100% of the disintegrations of ThC''; and note the branching decay of ThC.

We wish to discuss this decay sequence in more detail in the following pages, but we shall limit our remarks to those features which are definitely established and not try to review all the extensive literature on these nuclides. Not all the radiations are definitely assigned and there are conflicting reports concerning the existence or abundance of certain low intensity gamma rays and beta ray groups. Reference to a large number of research papers

Fig. 6.28. The growth of ThB (10.6 h, Pb$^{212}$) and ThC (60.5 m, Bi$^{212}$) into ThX (3.64 d, Ra$^{224}$).
Fig. 6.29. The growth of ThC (Bi$_{212}^+$) into pure ThB (Pb$_{212}^+$);

\[
\text{ThB} \xrightarrow{\beta} \frac{1}{10.6 \text{ hours}} \quad \text{ThC} \xrightarrow{\alpha \beta} \frac{1}{60.5 \text{ min.}}
\]

The growth curve for ThC' is identical in shape but rises only to 64% the activity of ThC because of the branching decay of ThC.
Table 6.21 Energies of Prominent Conversion Electrons in Th(B+C+C") Spectrum. K. Siegbahn and T.R. Gerholm

<table>
<thead>
<tr>
<th>Line</th>
<th>Electron Energy (keV)</th>
<th>Conversion Shell</th>
<th>Origin</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>24.509</td>
<td>LI</td>
<td>ThC_ThC&quot;</td>
<td>6</td>
</tr>
<tr>
<td>B</td>
<td>36.150</td>
<td>MI</td>
<td>ThC_ThC&quot;</td>
<td>4</td>
</tr>
<tr>
<td>F</td>
<td>148.108</td>
<td>K</td>
<td>ThB_ThC</td>
<td>200</td>
</tr>
<tr>
<td>I</td>
<td>222.22</td>
<td>LI</td>
<td>ThB_ThC</td>
<td>22</td>
</tr>
<tr>
<td>Ia</td>
<td>222.90</td>
<td>LII</td>
<td>ThB_ThC</td>
<td>1.4</td>
</tr>
<tr>
<td>J</td>
<td>234.61</td>
<td>MI or LI</td>
<td>ThB_ThC</td>
<td>6.0</td>
</tr>
<tr>
<td>L</td>
<td>422.84</td>
<td>K</td>
<td>ThC&quot;_ThD</td>
<td>1.4</td>
</tr>
<tr>
<td>X</td>
<td>2526.3</td>
<td>K</td>
<td>ThC&quot;_ThD</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Fig. 6.30. Decay schemes for the principal transitions in the "thorium active deposit" ThB $\beta \rightarrow$ ThC $\alpha$ ... Notice that the short-range $\alpha$ rays of ThC are $\alpha$ transitions to excited levels, while the long-range $\alpha$ rays of ThC' are $\alpha$ transitions from excited levels. Notice the origin of the very important and useful 2.62-MeV $\gamma$ ray, which is in cascade with a preceding 0.58-MeV $\gamma$ ray and the $\beta$ transition. When all $\alpha$, $\beta$ and $\gamma$-ray energies are summed, the total disintegration energy is the same (11.19 MeV) in the two competing branches ThC $\beta \rightarrow$ ThC' $\alpha \rightarrow$ ThD and ThC $\alpha \rightarrow$ ThC' $\beta \rightarrow$ ThD. The angular momentum and parity assignments in ThD are as determined by Elliott and coworkers.
published before 1958 can be found in the data compilation of STROMINGER, HOLLANDER and SEABORG,\textsuperscript{149} or in the LANDOLT-BÖRNSTEIN Tables,\textsuperscript{149a} or in the Nuclear Data Sheets published by the National Research Council.

Since 1956 a series of papers\textsuperscript{150-157} by Russian authors reporting from the Leningrad Institute of Railroad Engineering have given much valuable new information on the electron spectra of the thorium active deposit and has cleared up many of the discrepancies in the older literature. This work was supplemented by a careful study of external conversion lines made by EMERY and KANE \textsuperscript{158} and by a series of photon measurements and \(\alpha\)-\(\gamma\) coincidence measurements by SCHUPP ET AL.\textsuperscript{158a} and by V. HAUSER and W. KERLER.\textsuperscript{158b}

The Decay of Thorium B (\(\text{Po}^{212}\)). The rather simple decay scheme of Thorium B is shown in Fig. 6.31. This scheme, which follows closely that

\begin{itemize}
  \item \textsuperscript{149} See Table of Isotopes by D. Strominger, J.M. Hollander, and G.T. Seaborg, Rev. Mod. Phys. (1958).
  \item \textsuperscript{153} A.I. Zhernovoi et al., Zhur. Eksp. i Teoret. Fiz. 32, 682 (1957); [translation: Soviet Phys. JETP 5, 563 (1958)].
  \item \textsuperscript{154} E.M. Krisyuk et al., Nucl. Phys. 4, 579 (1957).
  \item \textsuperscript{155} E.M. Krisyuk et al., Zhur Eksp i Teoret. Fiz. 33, 1144 (1957); [translation: Soviet Phys. JETP 6, (33), 880 (1958)].
  \item \textsuperscript{156} A.G. Sergeev et al., Zhur. Eksp. i Teoret. Fiz. 33, 1140 (1957); [translation: Soviet Phys. JETP 6, (33) 878 (1958)].
  \item \textsuperscript{158} G.T. Emery and W.R. Kane, Phys. Rev. 118, 755 (1960); see also G.T. Emery, Atomic Energy Commission document, AECU-4169 (1958).
  \item \textsuperscript{158a} G. Schupp, H. Daniel, G.W. Eakins and E.N. Jensen, Phys. Rev. 120, 189 (1960).
  \item \textsuperscript{158b} V. Hauser and W. Kerler, Z. Physik 158, 405 (1960).
Fig. 6.31. Decay scheme of Thorium B (Pb$^{212}$) as drawn by KRUSYOUK et al.\textsuperscript{154} The gamma transitions are labeled by the classical nomenclature of Ellis. The spins of the upper two levels are those suggested by ROETLING et al.\textsuperscript{158a}
given by ELLIS in 1934, is taken from the work of KRISYUK, SERGEYEV, LATYSHEV and VOROBYOV except for the spin assignment of the upper two levels for which the $\gamma\gamma$ angular correlation experiments of ROETLING, GANLEY and KLAIBER specify spins at variance with those given by KRISYUK ET AL. This scheme includes all the gamma rays known with certainty to occur in the decay of Pb$^{212}$. The level at 415.3 keV decays by a direct gamma transition to ground and also by two gamma ray cascades; the energy sums of the cascades are equal to the energy of the ground state transition to well within the small experimental error.

The spin assignment of 1 with negative parity to the ground state of Bi$^{212}$ comes from the work of HORTON who measured the $\alpha\gamma$ angular correlation in Bi$^{212}$ $\alpha$-decay and analyzed the log ft data in Bi$^{212}$ $\beta$-decay. The spin assignments of the upper states come from the multipolarity determinations of the gamma rays and from arguments based on log ft values and $\gamma\gamma$ angular correlations.

Bi$^{212}$ has one proton and three neutrons beyond closed shell configurations and one might expect the shell model to provide an explanation of the spin sequence observed in the level system and of the intensity pattern in the gamma rays. KRISYUK and CO-WORKERS and WALEN and BASTIN speculate on the shell model interpretation but arrive at somewhat different conclusions.

Direct measurement and resolution of the beta spectrum of Pb$^{212}$ was carried out by MARTIN and RICHARDSON who reported groups at 331 and 569 keV and by FEATHER, KYLES and PRINGLE who reported the values 355 and 589 keV. The gamma ray studies indicate that lower-energy beta groups must be present in lower intensity as is indicated in the figure.

The Decay of Thorium C (Bi$^{212}$). Thorium C resembles radium C of the uranium series and actinium C of the actinouranium series by decaying partially by alpha emission and partially by beta emission. In the case of thorium C

the alpha branching is 36 percent. The alpha branch of the thorium C decay scheme is shown in Fig. 6.31. The alpha particle energies and abundances are taken from the work of RYTZ\textsuperscript{163} and of WALEN and BASTIN\textsuperscript{160} and of LEANG.\textsuperscript{163a} Some evidence obtained by alpha-gamma coincidence measurements are supplied by BERTOLINI and CO-WORKERS.\textsuperscript{166a} Gamma rays with the energies 40, 144, 164, 288, 328, 432, 352, 472 MeV and others have been reported by SURUGUE\textsuperscript{164} and by others. The most prominent gamma transition is the 40 keV transition dropping from the first excited state of Tl\textsuperscript{208}. The energy of this transition has been precisely measured\textsuperscript{151,153,165} as 39.85 keV. From the L\textsubscript{I}, L\textsubscript{II}, L\textsubscript{III} conversion ratios it is clear that this transition is magnetic dipole radiation (M1). NIELSEN's\textsuperscript{166} measurements on the other gamma rays shown in Fig. 6.32 prove that they also are magnetic dipole in character. The daughter nucleus Tl\textsuperscript{208} is but one proton and one neutron removed from a double closed shell so that theoretical prediction of the low lying levels should be possible from shell model theory. PRYCE\textsuperscript{167} proposed the spin assignments 5+ and 4+ for the ground state and first excited state. These assignments are supported by the alpha-gamma angular correlation studies and analysis of HORTON,\textsuperscript{159} at least as far as the spin and parity are concerned. PRYCE suggests that the next four levels are a quartet arising from the (d\textsubscript{3/2})\textsuperscript{-1} (g\textsubscript{9/2})\textsubscript{n} configuration and having 3-, 6-, 4- and 5- ascending in that order. NIELSEN'S\textsuperscript{166} results are consistent with PRYCE'S spin predictions for the 327 and 471 keV levels but are inconsistent with the prediction of spin 6 for the 492 keV level. The alpha decay of B\textsubscript{121} is hindered by a factor of about 3 x 10\textsuperscript{44} for decay to the ground state and to the first excited state when compared to decay rates observed in even-even nuclei. HORTON'S\textsuperscript{159} results on the α-40 keV γ anisotropy indicate that the alpha wave leading to the first excited state is a pure L = 3 wave or a nearly pure L = 5 wave. These results support the spin and parity assignments

\textsuperscript{163} A. Rytz, Compt. rendu. 233, 790 (1951).
\textsuperscript{163a} Leang Chin-Fan, Thesis, Paris 1962 as reported to the author by R.J. Walen.
Fig. 6.32. Alpha branch decay scheme of ThC (Bi\textsuperscript{212}). ThC decays 36 percent by alpha emission. The alpha energies and intensity figures are taken from Walen and Bastin and Leang Chin-Fan.
and help to explain the large hindrance factors. See the discussion of Horton\textsuperscript{158} and of Perlman and Rasmussen.\textsuperscript{168}

Further discussion of the difficulties of providing a shell model interpretation of the energy levels and of the alpha intensity pattern is given by Walen and Bastin.\textsuperscript{160}

We not turn to a consideration of the beta branching decay of thorium C. The complex gamma spectrum accompanying this decay has been studied by many authors,\textsuperscript{151-158, 166a, 169-75, 176abcd} but unfortunately the published reports contain many contradictory data. It seems clear that in some cases gamma rays belonging to other members of the thorium active deposit or to members of the radium decay chain, present as an impurity in the samples under study, were falsely assigned to thorium C. In the summary presented here the conclusions of Emery and Kane\textsuperscript{158} and of Sergeev and co-workers\textsuperscript{156} are followed. These are re-enforced, except for one spin assignment, by the work of Schupp et al.,\textsuperscript{158a} of Hauser and Kerler\textsuperscript{158b} or Giannini, Prosperi and Aciuti\textsuperscript{176a} and of Gangrskii, Gusinskii and Lemberg.\textsuperscript{176b}

\textsuperscript{169}. G.D. Latsyshev, Rev. Mod. Phys. 19, 132 (1947).
\textsuperscript{170}. A. Johansson, Arkiv F. Mat. Astr. Fysik A34, 9 (1947).
\textsuperscript{173}. B. Chinaglen and F. Demichelis, Nuovo Cimento 4, 1160 (1956).
\textsuperscript{174}. A.I. Alichanian and V.P. Dzelepov, Compt. rend. Acad. Soc. USSR 20, 115 (1938).
\textsuperscript{176d}. Schupp, Daniel, Eakins and Jensen, Phys. Rev. 120, 189 (1960).
The electromagnetic transitions occurring between levels of the Po\(^{212}\) nucleus are summarized in Table 6.22. In order to place these transitions in a decay scheme one can first construct a skeleton level system from the data on the long-range alpha particles of Radium C'. Our knowledge of these comes from the careful work of LEWIS and BOWDEN\(^{177}\) and of RYTZ\(^{163}\) as reviewed by BRIGGS.\(^{178}\) The three long-range \(\alpha\)-groups define levels at 727, 1680, and 1800 keV in Po\(^{212}\). It is possible to fit six of the observed gamma rays into the decay scheme as transitions between these levels or between one of those levels and the ground state. The other \(\gamma\)-transitions indicate a need to postulate levels at 1620 and 1513 keV.\(^{156}\) The decay scheme constructed in this way is shown in Fig. 6.23. The beta intensity figures given in this figure are those estimated by EMERY and KANE from a consideration of the gamma ray intensities. The beta groups and the corresponding log \(f_t\) values are summarized in Table 6.22. The log \(f_t\) are all consistent with first forbidden transitions, as they must be if the spin assignments are correct.

EMERY and KANE\(^{158}\) call attention to the fact that the level scheme of Po\(^{212}\) bears a close similarity to the lower levels of Po\(^{214}\) as displayed in Fig. 6.14. In the discussion of the decay scheme of radium C' (Bi\(^{214}\)) appearing earlier in this chapter, it is mentioned that the first excited 2+ level and a second 2+ level lying at little more than twice the energy of the first 2+ state may constitute a one phonon and two phonon excitation of a collective quadrupole vibrational motion about an equilibrium spherical shape. One important characteristic of such a series of levels is that the second 2+ state de-excites by a cascade of two \(E2\) transitions and does not de-excite by a direct \(E2\) transition to the ground state. Such a pattern of decay appears here in the Po\(^{212}\) level system.

A more correct interpretation of the low-lying levels of Po\(^{212}\) may be the one provided by the calculations of BAND, Kharitonov, and SLIV\(^{178a}\) and of GLENDENNING.\(^{178d}\) These authors consider the possible shell model wave functions for the two protons and the two neutrons which are added to the Po\(^{208}\) closed shell core to construct the Po\(^{212}\) nucleus. The residual forces working

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### Table 6.22 Electromagnetic Transitions in Po$^{212}$

Table reproduced from Emery and Kane, Phys. Rev. 118, 755 (1960).

<table>
<thead>
<tr>
<th>Gamma$^a$</th>
<th>$E$ (keV)</th>
<th>$I_\gamma$(%)$^b$</th>
<th>$I_\gamma$(%)</th>
<th>$\epsilon_k$</th>
<th>Multipolarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>727</td>
<td>0.106</td>
<td>10.1±0.6</td>
<td>0.0105±0.008</td>
<td>E2</td>
</tr>
<tr>
<td>0a</td>
<td>785</td>
<td>0.051</td>
<td>1.5±0.3</td>
<td>0.034±0.008</td>
<td>M1</td>
</tr>
<tr>
<td>Pa</td>
<td>893</td>
<td>0.014</td>
<td>0.6±0.3</td>
<td>0.023±0.012</td>
<td>M1</td>
</tr>
<tr>
<td>Pa2a</td>
<td>953</td>
<td>0.010</td>
<td>≤ 0.8</td>
<td>≥ 0.009</td>
<td>(M1 + E2)</td>
</tr>
<tr>
<td>R</td>
<td>1074</td>
<td>0.006</td>
<td></td>
<td></td>
<td>(E2)</td>
</tr>
<tr>
<td>Ra</td>
<td>1078</td>
<td>0.014</td>
<td>1.0±0.2</td>
<td></td>
<td>---</td>
</tr>
<tr>
<td>---</td>
<td>1350</td>
<td>---</td>
<td>≤ 0.33</td>
<td></td>
<td>---</td>
</tr>
<tr>
<td>S</td>
<td>1513</td>
<td>0.008</td>
<td>≤ 0.7</td>
<td>≥ 0.008</td>
<td>?</td>
</tr>
<tr>
<td>Sa</td>
<td>1620</td>
<td>0.013</td>
<td>2.6±0.4</td>
<td>0.0050±0.0015</td>
<td>M1</td>
</tr>
<tr>
<td>---</td>
<td>1680</td>
<td>---</td>
<td>≤ 0.4</td>
<td></td>
<td>---</td>
</tr>
<tr>
<td>Sb</td>
<td>1800</td>
<td>0.007</td>
<td>≤ 0.4</td>
<td>≥ 0.012</td>
<td>E0$^c$</td>
</tr>
<tr>
<td>---</td>
<td>2200</td>
<td>---</td>
<td>≤ 0.27</td>
<td></td>
<td>---</td>
</tr>
</tbody>
</table>

Intensities are given in percent of the decays of Bi$^{212}$ to Po$^{212}$.  

$\epsilon_k$ is the K-conversion coefficient.

$^a$The letter designations follow the classical nomenclature.

$^b$These figures come from the Russian literature.

$^c$Schupp, Daniel, Eakins and Jensen (Phys. Rev. 120, 189 (1960)) present a table with values in rather good agreement with Emery and Kane, but there is a major discrepancy in the multipolarity assignment of the 1800 keV gamma. In an $\alpha\gamma$ coincidence experiment Schupp et al. saw photons of 1800 keV energy and assigned a multipolarity of E2 to the transition. Their result is confirmed by Hauser and Kerler, Z. Physik 158, 405 (1960) and others.
## Part II

### Table 6.22 Beta Transitions from Bi\textsuperscript{212} to Po\textsuperscript{212}

<table>
<thead>
<tr>
<th>Energy of Excited State (MeV)</th>
<th>Maximum Energy of betas (MeV)</th>
<th>Intensity in percent</th>
<th>log ft</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.25</td>
<td>86</td>
<td>7.3</td>
</tr>
<tr>
<td>0.727</td>
<td>1.52</td>
<td>7</td>
<td>7.7</td>
</tr>
<tr>
<td>1.513</td>
<td>0.74</td>
<td>~2</td>
<td>~7.1</td>
</tr>
<tr>
<td>1.620</td>
<td>0.63</td>
<td>~3.2</td>
<td>~6.6</td>
</tr>
<tr>
<td>1.680</td>
<td>0.57</td>
<td>&lt;1.2</td>
<td>&gt;7.0</td>
</tr>
<tr>
<td>1.800</td>
<td>0.45</td>
<td>~1.2</td>
<td>~6.7</td>
</tr>
</tbody>
</table>

The branch intensities are derived from the gamma-ray intensities.

From G.T. Emery and W.R. Kane, Phys. Rev. 118, 755 (1960); for another slightly different set of intensities and ft values see Gangrskii, Gusinskii and Lemberg.
between nn, pp and pn pairs strongly influence the properties of the levels. The interaction of the four external particles with surface oscillations also influence the results somewhat but these collective oscillations are not a dominant feature of the lowest levels. The theoretical spectrum can account for the spin and parity assignments of the chief levels seen in the decay of ThC and for the characteristics of the γ-rays de-exciting these levels.

The most prominent gamma ray in the beta decay of thorium B is the 727 keV transition from the first excited state at 2+ to the ground state. This is thoroughly characterized as electric quadrupole by its K/L conversion ratio and its total conversion coefficient. The Ten-fold increase of the reduced transition probability B(\(E2\)) over the "single proton" value has been cited\(^\text{158}\) as evidence of the collective nature of this transition, but the wave functions of BAND, KHIRITONOV and SLIV\(^\text{178a}\) also account for the enhancement in rate while assigning a completely different nature to the 727 keV 2+ level.

The Decay of Thorium C' (Po\(^{212}\)). ThC' (Po\(^{212}\)) decays with the emission of 8.780 MeV alpha particles. The half-life of 3.04 x 10\(^{-7}\) seconds has been measured by delayed coincidence methods. The alpha particles of ThC' are the most energetic among the naturally occurring isotopes (except for low intensity long-range alphas of ThO and RaC') and the alpha particle energy has been measured with great accuracy.\(^\text{178,178b}\) It is currently used as one of the absolute alpha standards in the calibration of magnetic spectrometers.

The decay scheme of ThC' is characterized by the appearance of long-range alpha groups whose origin is best understood by reference to Fig. 6.33. Excited levels in ThC' de-excite by alpha emission to the ground state of ThD. Alpha emission from an excited state is a very rare occurrence and among all the naturally occurring radioelements the only other isotope in which it is observed is RaC'. Usually gamma emission to the ground state occurs so much more readily that alpha emission, a relatively slow process, cannot compete. In ThC' and RaC', however, the alpha disintegration energy is so large that the alpha decay half-life becomes short enough to compete with gamma emission.

\(^{178b}\) Unfortunately more recent determinations have been about 5.5 keV higher in energy so that there remains some doubt about the correct energy of this important standard; Collins et al., Proc. Roy. Soc. (London) A216, 219 (1953) give 8.7857 ± 0.004 while Rytz, Helv. Phys. Acta. 34, 240 (1961) gives 8.7854 ± 0.008.
Fig. 6.33. Beta branch decay scheme of ThC (Bi$^{212}$). The ThC decays 64 percent by beta emission. The level scheme of Po$^{212}$ is that published by Russian authors. The beta group intensities are those deduced by Emergy and Kane from their $\gamma$-intensity figures. The data on long range alphas come from the work of Lewis and Bowden and of Rytz. According to Schupp, Daniel, Eakins and Jensen the 1800 keV level is 2+ and the 1800 keV transition is E2. Additional gamma rays are reported by Giannini, Prosperi and Sciuti.
and the excited states show branching decay by alpha emission to a significant degree. For every 10,000 alpha particles representing decay from the ground state of ThC' there are 230 long-range alpha particles representing decay from excited states.

Isomeric form of Po$^{212}$. By reactions of artificial transmutation PERLMAN, ASARO, GHIORSO, LARSH and LATIMER$^{178c}$ have prepared and identified an isomeric form of ThC' with exceedingly interesting properties. This isomer does not occur in natural radioactivity, but we find it convenient to discuss it here.

The isomer is most conveniently prepared by helium ion bombardments of bismuth but it was first discovered in irradiations of bismuth and lead targets with more complex particles such as accelerated ions of $^{12}C$, $^{10}B$, and $^{16}O$. The most prominent radiation emitted by the isomer is an alpha particle group with the large energy of $11.65 \pm 0.02$ MeV and a half-life of 45 seconds. Two other alpha groups were identified: $9.08 \pm 0.015$ MeV (1% intensity) and $8.52 \pm 0.015$ MeV (2.05 \( \pm \) 0.09% intensity). These energies are all relative to At$^{211}$ and Po$^{211}$ standards taken as 5.862 MeV and 8.780 MeV, respectively. By alpha-gamma coincidence measurements the presence of a 0.57 MeV gamma ray in ~2 percent intensity and a 2.61 MeV gamma ray in 2.6 percent intensity was established. These results led to the decay scheme shown in the figure. It is seen that excited levels of Po$^{208}$ are populated at 2.61 and 3.19 MeV. These levels are known to exist from previous work on the decay of ThC'' (Tl$^{208}$); see Fig. 6.34. No radiations indicating an isomeric transition of Po$^{212m}$ to the ground state were observed.

This is an extraordinary instance of alpha decay because a half-life of 45 seconds for an 11.65 MeV alpha group implies a hindrance in the alpha emission process by a factor of $10^{13}$. This implies an unusual structure and high angular momentum for Po$^{212m}$ and a severe restriction on the possible excited states of Po$^{212}$ which lie between Po$^{212m}$ and the ground state. Po$^{212}$ is an even-even nucleus with 2 protons and 2 neutrons beyond Po$^{208}$, which has a particularly stable configuration. In the Po$^{212}$ ground state the 2 neutrons and 2 protons are paired off to a net spin of zero. In its excited states,

Decay scheme of Po$^{212}$ isomers.
however, these four nucleons, which individually have high intrinsic spin, can recouple in various ways to give very high resultant spin. In order to predict the spectrum of levels expected from this recoupling one must assume some definite form for the residual interaction between the nucleons and carry through a detailed calculation. This has been done by GLENDENNING\textsuperscript{178d} who concludes that the most important particle configuration is \((h_2/2, g_2/2)\) and that the sequence of levels in order of energy is \(0^+, 2^+, 4^+, 6^+, 8^+, 10^+, 18^+, 16^+\), etc. The isomerism is identified with the 18\(^+\) state which has a "spin gap" of 8 between itself and the state of highest spin lying beneath it.

\[\text{ThC}^\prime\prime\left(\text{Tl}^{208}\right)\]. The decay of 3.1 minute \text{ThC}^\prime\prime is shown in Fig. 6.34.

One of the features of principal interest is the very high energy gamma ray of 2.615 MeV which occurs in 100 percent abundance. This is the most energetic gamma ray to be found among the natural radioactivities. It is commonly used as a standard to calibrate gamma ray or electron spectrometers. The photons can be used to calibrate a scintillation spectrometer and since the K conversion coefficient is 0.0018 an appreciable number of mono-energetic electrons of 2.526 MeV energy are available for calibration of electron spectrometers. For this purpose one prepares an intense source of the thorium active deposit.

Several investigations which led to the decay scheme shown in Fig. 6.34 may be mentioned. MARTIN and RICHARDSON\textsuperscript{179,180} made an analysis of the energies and intensities of the gamma ray and beta particles and established the existence of excited levels at 2.62, 3.20, 3.48 and 3.71 MeV. There was considerable uncertainty about the spin and parity assignments of these levels until definite choices were made by ELLIOTT, GRAHAM, WALKER and WOLFSON\textsuperscript{181} on the basis of gamma-gamma angular correlation experiments and conversion coefficients. The unique shape of the correlation between the prominent 583 keV and 2.615 MeV gamma rays is quite strong evidence for the 5 - 3 - 0 sequence; in particular, the 4 - 2 - 0 sequence which one might have expected is definitely ruled out. Additional gamma rays reported by ELLIOTT ET AL.\textsuperscript{181} and confirmed

\begin{itemize}
\item \textsuperscript{178d.} N.K. Glendenning, Phys. Rev. 127, 923 (1962).
\item \textsuperscript{179.} H.O.W Richardson, Nature 161, 516 (1948).
\item \textsuperscript{180.} D.G.E. Martin and H.O.W. Richardson, Proc. Phys. Soc. 60, 466 (1948).
\end{itemize}
Fig. 6.34. Decay scheme of Thorium C" (Tl$^{208}$). All energies are given in keV. Gamma intensities in percent are given beneath the arrow tips. See also Tables 6.23 and 6.24.
by KRISYUK ET AL.\textsuperscript{155} establish the existence of a further level at 3.961 which most probably has the spin 6. EMERY and KANE\textsuperscript{158} measured the intensity of the photons emitted in the decay of thorium C\textsuperscript{11} by an external conversion technique and combined their results with the internal conversion measurements of KRISYUK ET AL.\textsuperscript{155} to arrive at the intensity figures summarized in Table 6.23. They used these gamma ray intensity figures to compute the beta ray spectrum and \( |f| \) values summarized in Table 6.24. SCHUPP, DANIEL, EAKINS and JENSEN\textsuperscript{158b} have made a similar analysis based on their \( \beta-\gamma \) coincidence and \( \gamma \)-intensity data. WOOD and JASTRAM\textsuperscript{180a} reinvestigated the spin and parity assignments of the levels by means of a combination of polarization-correlation and directional-correlation measurements.

Several authors\textsuperscript{159,155,167} have chosen 5 as the most likely spin for the ground state of thorium C\textsuperscript{11}.

The level scheme of Pb\textsuperscript{208} is anomalous for an even-even nucleus and has excited the interest of the theorists of nuclear structure. A discussion of the possible interpretations is given in Sec. 10.2.2 of Chapter 10.

\textsuperscript{180a} G.T. Wood and P.S. Jastram, Nuclear Physics 32, 411 (1962).
Table 6.23 Electromagnetic Transitions in Pb\textsuperscript{208} from Decay of Tl\textsuperscript{208}

<table>
<thead>
<tr>
<th>Gamma</th>
<th>E(keV)</th>
<th>Electron Intensity I\textsubscript{k} (%)\textsuperscript{a}</th>
<th>Photon Intensity I\textsubscript{\gamma} (%)\textsuperscript{b}</th>
<th>(\varepsilon\textsubscript{k})</th>
<th>Multipolarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>E\textsubscript{c}</td>
<td>211</td>
<td>0.15</td>
<td>-----</td>
<td>-----</td>
<td>(M\textsubscript{1})</td>
</tr>
<tr>
<td>E\textsubscript{d}</td>
<td>233</td>
<td>0.13</td>
<td>-----</td>
<td>-----</td>
<td>(M\textsubscript{1})</td>
</tr>
<tr>
<td>F\textsubscript{b}</td>
<td>252</td>
<td>0.37</td>
<td>1.5(\pm)0.7</td>
<td>0.25(\pm)0.15</td>
<td>(M\textsubscript{1})</td>
</tr>
<tr>
<td>G</td>
<td>277</td>
<td>2.4</td>
<td>6.9(\pm)1.2</td>
<td>0.35(\pm)0.06</td>
<td>M\textsubscript{1}</td>
</tr>
<tr>
<td>J\textsubscript{c7}</td>
<td>486</td>
<td>0.01</td>
<td>-----</td>
<td>-----</td>
<td>(E\textsubscript{2})</td>
</tr>
<tr>
<td>L</td>
<td>511</td>
<td>1.7</td>
<td>23.0(\pm)2.0</td>
<td>0.074(\pm)0.007</td>
<td>M\textsubscript{1}\textsuperscript{E2\textsuperscript{e}}</td>
</tr>
<tr>
<td>M</td>
<td>583</td>
<td>-----</td>
<td>86.4(\pm)5.6</td>
<td>0.0156\textsuperscript{c}</td>
<td>E\textsubscript{2}</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>763</td>
<td>0.058</td>
<td>1.9(\pm)0.5</td>
<td>0.031(\pm)0.008</td>
<td>M\textsubscript{1}</td>
</tr>
<tr>
<td>P</td>
<td>860</td>
<td>0.27</td>
<td>11.4(\pm)1.2</td>
<td>0.024(\pm)0.003</td>
<td>M\textsubscript{1}</td>
</tr>
<tr>
<td>X</td>
<td>2614</td>
<td>0.17</td>
<td>(100)</td>
<td>(0.0017)\textsuperscript{a,c,d}</td>
<td>E\textsubscript{3}</td>
</tr>
</tbody>
</table>

Intensities are given in percent of Tl\textsuperscript{208} decays. The classical letter designations are given in the first column. \(\varepsilon\textsubscript{k}\) is the K-conversion coefficient.

\textsuperscript{a} Krisyuk\textsuperscript{155} et al.
\textsuperscript{b} Emery and Kane\textsuperscript{158}.
\textsuperscript{c} Elliott et al.\textsuperscript{181}.
\textsuperscript{d} Alichianian and Nikitin, Phys. Rev. \textbf{53}, 767 (1938).
\textsuperscript{e} Various authors have given differing values of the multipole mixing of the 511 keV transition: Elliott et al. reported the intensity ratio of E\textsubscript{2} to M\textsubscript{1} as 1.7\(\pm\)0.3 and later as 1.0\(\pm\)0.4; Wood and Jastron (Nuclear Physics \textbf{32}, 411 (1962)) reported a ratio 0.18\(\pm\)0.03 and Emery and Kane\textsuperscript{158} give 0.18\(\pm\)0.15.
Table 6.24 Beta Transitions from Thallium-208 to Lead-208

<table>
<thead>
<tr>
<th>Energy of Excited State (MeV)</th>
<th>Maximum Energy of Betas (MeV)</th>
<th>Emery and Kane Intensity in Percent</th>
<th>Schupp et al. Intensity in Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.62</td>
<td>2.38</td>
<td>~0.03 *</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>3.20</td>
<td>1.80</td>
<td>51.3</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>48.8</td>
</tr>
<tr>
<td>3.48</td>
<td>1.52</td>
<td>20.6</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>22.7</td>
</tr>
<tr>
<td>3.71</td>
<td>1.28</td>
<td>24.3</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>23.9</td>
</tr>
<tr>
<td>3.96</td>
<td>1.03</td>
<td>3.6</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.6</td>
</tr>
</tbody>
</table>

*This figure comes from unpublished work of Elliott and co-workers.*
6.4 THE ACTINIUM (4n+3) SERIES

We have discussed the uranium-radium and the thorium series in the preceding sections of this chapter and now turn to a consideration of the third family of heavy element radioactive elements, the series known as the actinium series or, alternatively, as the actinouranium series.

The actinium decay chain is summarized in Fig. 6.35 and in Table 6.25.

**Uranium-235.** The primary activity from which all the other (secondary) activities in the actinium series are derived is U$^{235}$. It is entirely possible that higher-mass nuclides in the 4n+3 family - nuclides such as Pu$^{239}$, Cm$^{243}$, Am$^{243}$, Bk$^{247}$, etc - were also present when the elements were first formed, but only U$^{235}$ of all the nuclides of the 4n+3 mass type above the element lead, is sufficiently long-lived to have persisted throughout geologic time. The half-life of U$^{235}$ is $7.13 \times 10^8$ years. Any sample of natural uranium no matter what its source contains U$^{235}$ in a constant amount, namely 0.720 atom percent or 0.711 weight percent. We have discussed natural uranium and the determination of the specific activity of uranium isotopes in Sec. 6.2. See particularly Table 6.2.

Because of the constant amount of U$^{235}$ in natural uranium the amount of protactinium, actinium, etc. found in uranium minerals bears a constant ratio to the total uranium content and to the members of the uranium-radium decay chain as we have seen in Table 6.3. This fact was noted early in the study of the natural radioactivities and led to some confusion. For many years it was believed that actinium must be a member of the uranium-radium decay series as a result of a branching decay somewhere near the beginning of this series, perhaps at Uranium I or Uranium II. This confusion was understandable because U$^{235}$ was not discovered until the mass-spectrographic work of DEMPSTER in 1935 and because no member of the actinium series could be isolated in sufficient amount and isotopic purity for an accurate atomic weight determination. It was not until 1935 that A.V. GROSSE measured the atomic weight of protactinium by weighing a pure compound of known composition.

Uranium-235 is an alpha emitter with a complex alpha spectrum and a complex gamma spectrum. These radiations and the decay scheme are thoroughly discussed in Sec. 8.4.8 of Chapter 8.
Table 6.25 The Actinium Series

<table>
<thead>
<tr>
<th>Radioelement</th>
<th>Symbol</th>
<th>Radiation</th>
<th>Half-life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actinouranium</td>
<td>U²³⁵</td>
<td>α</td>
<td>7.13 x 10⁸ y</td>
</tr>
<tr>
<td>Uranium Y</td>
<td>Th²³³</td>
<td>β</td>
<td>25.64 h</td>
</tr>
<tr>
<td>Protactinium</td>
<td>Pa²³²</td>
<td>α</td>
<td>3.48 x 10⁴ y</td>
</tr>
<tr>
<td>Actinium</td>
<td>Ac²²⁷</td>
<td>β and α</td>
<td>22.0 y</td>
</tr>
<tr>
<td>Radioactinium</td>
<td>Th²²⁷</td>
<td>α</td>
<td>18.17 d</td>
</tr>
<tr>
<td>*Actinium K</td>
<td>Fr²²³</td>
<td>β</td>
<td>21 m</td>
</tr>
<tr>
<td>Actinium X</td>
<td>Ra²²³</td>
<td>α</td>
<td>11.68 d</td>
</tr>
<tr>
<td>Actinon</td>
<td>Em²¹⁹</td>
<td>α</td>
<td>3.92 s</td>
</tr>
<tr>
<td>Actinium A</td>
<td>Po²¹⁵</td>
<td>α</td>
<td>1.83 x 10⁻³ s</td>
</tr>
<tr>
<td>Actinium B</td>
<td>Pb²¹¹</td>
<td>β</td>
<td>36.1 m</td>
</tr>
<tr>
<td>Actinium C</td>
<td>Bi²¹¹</td>
<td>β and α</td>
<td>2.16 m</td>
</tr>
<tr>
<td>Actinium C'</td>
<td>Po²¹¹</td>
<td>α</td>
<td>.52 s</td>
</tr>
<tr>
<td>Actinium C&quot;</td>
<td>Tl²⁰⁷</td>
<td>β</td>
<td>4.79 m</td>
</tr>
<tr>
<td>Actinium D</td>
<td>Pb²⁰⁷</td>
<td>stable</td>
<td></td>
</tr>
</tbody>
</table>

*.004% α-branching of AcK not shown; see Fig. 6.35.
Fig. 6.35. The actinium \((4n+3)\) series.
The fissionability of $^{235}$U and the characteristics of the fission process are described in detail in Chapter 11.

**Uranium-Y ($^{231}$Th).** The immediate decay product of $^{235}$U is 25.6 hour uranium-Y, an isotope of thorium. Uranium-Y is a beta emitter with a complex decay scheme which is thoroughly discussed in Sec. 8.2.10 of Chapter 8. The most energetic beta group has an energy of 300 keV and the total decay energy is 383 keV.

Uranium-Y can be isolated from isotopically-pure $^{235}$U after a few days growth period. If it is necessary to prepare UY samples from natural uranium, the samples will be contaminated with UX$_1$ and UX$_2$ since in each milligram of natural uranium there are 733.6 disintegrations per minute of UX$_1$ and UX$_2$ and 33.7 disintegrations per minute of UY. This ratio can be improved somewhat in favor of UY by purifying the uranium from thorium, waiting a few hours or a day and then isolating a UY fraction before much UX has had a chance to grow in. To prepare samples for beta spectrometric studies a better approach is to prepare Th$^{231}$ artificially by neutron bombardment of ionium$^{182}$ or of thorium.$^{183}$

$$\text{I}^{230} \ (n,\gamma) \ \text{Th}^{231}$$

$$\sigma = 26 \text{ barns}$$

$$\text{Th}^{232} \ (n,2n) \ \text{Th}^{231}$$

**Protactinium.** Protactinium was discovered by HAHN and MEITNER in 1918 and almost simultaneously by SODDY and CRANSTON. A.V. GROSSE, who made many early contributions to the chemistry of this element, prepared the first pure compound in 1927.

Protactinium is an alpha emitter with a half-life of 34,800 years as determined by specific activity measurements on a weighed sample of pure ignited protactinium oxide. The value of $34,300 \pm 300$ years quoted by VAN WINKLE, LARSON and KATZIN$^{184}$ is based on the formula Pa$_2$O$_5$. Using later information

that the ignited oxide corresponds more closely to $\text{Pa}_2\text{O}_5$. Elson\textsuperscript{185} recalculated the value $34,800 \pm 300$ years. Protactinium-231 is the longest-lived of the isotopes of element 91 and the only isotope suitable for the isolation of the element in weighable quantities. The name protactinium was given to $\text{Pa}^{231}$ by Hahn and Meitner because it was the long-sought-for progenitor of actinium. The name has since been taken over as the name of the element and all its isotopes. An earlier spelling, protoactinium, has been shortened to protactinium.

Because of its origin as a decay product of $\text{U}^{235}$, protactinium is found only in uranium ores where its equilibrium concentration is only 343 milligrams per metric ton of natural uranium or almost exactly the same concentration as that of the rare element, radium. If one starts with a pure sample of $\text{U}^{235}$, protactinium will grow in at the rate shown in Fig. 6.36. Samples of protactinium ranging in size from milligrams to grams have been isolated from uranium ores but the chemical properties of protactinium are such that its isolation is a matter of considerable difficulty. In 1961 it was revealed by English government authorities that English scientists and engineers had succeeded in isolating the large quantity of 150 grams of protactinium from 60 tons of raffinate wastes of a uranium solvent extraction process.\textsuperscript{185a} It is also possible to synthesize protactinium by the neutron irradiation of ionium as is described earlier in this chapter in the ionium part of Sec. 6.2.

The alpha and gamma spectra of protactinium, in common with that of most of the alpha emitters in the actinium series, are quite complex. These spectra and the decay scheme of $\text{Pa}^{231}$ are thoroughly discussed in Sec. 8.3.7. of Chapter 8.

**Early Difficulties in the Study of Actinium.** From the historical standpoint actinium is the most important member of the $4n+3$ series. The discovery and the early study of actinium were greatly hampered by difficulties arising from the following unfortunate circumstances.

1. The equilibrium amount of actinium in uranium ores is very small; the ratio of $\text{Ac}^{227}$ to normal uranium is $0.21 \times 10^{-9}$; the amount of $\text{Ac}^{227}$ in pitchblende is only $0.25 \times 10^{-5}$ of the amount of $\text{Ra}^{226}$ present.

---


Fig. 6.36. Growth of $^{231}\text{Pa}$ and $^{227}\text{Ac}$ into pure $^{235}\text{U}$. Half-life values used are those listed in Table 6.25.
(2) Actinium resembles the rare-earth elements closely in its chemical properties and is separated with difficulty from them. Uranium ores almost invariably contain considerable quantities of rare-earth impurities which are concentrated with the actinium.

(3) Actinium itself has very weak radiations and, in fact, for some years it was thought that actinium was "rayless". After 1911 it was recognized from the "displacement laws" that actinium must be a beta emitter, but it was not until 1935 that HULL, LIBBY and LATIMER detected electrons emitted by actinium. Even then, in view of knowledge obtained later on the alpha branching of actinium to AcK, it seems probable that these investigators may have been observing the beta particles of AcK. The end point energy of the Ac$^{227}$ beta particles is only 45 keV. The most energetic beta rays are stopped completely in an absorber of three milligrams per cm$^2$ and the majority of the electrons in the spectrum are stopped by less matter than that. When actinium is mixed with rare earth or other carrier material, the beta particles are almost completely absorbed within the sample itself.

The difficulties (1), (2) and (3) listed above still apply today and have hindered the detailed study of the properties of this interesting element. During the first years in which actinium was studied, the confusion was naturally greater because the daughter products were not known. The direct decay products, radioactinium and actinium-X, were first discovered with certainty 6 and 7 years, respectively, after the discovery of actinium. Furthermore, ionium was not discovered until 1907 and it was frequently a contaminant of actinium preparations because of the similar behavior of actinium and ionium in many chemical separations. This contamination had a curious result in the period 1905-1907 when actinium received consideration as the possible missing parent of the element radium. Proof of the formation of radium from actinium preparation was sought and was in fact found. Later, however, it became apparent that the radium formation was caused by ionium contamination in the actinium.

DEBIERNE in 1899 found that after the complete removal of uranium, 

polonium, and radium from pitchblende solutions it was possible to precipitate a mixed hydroxide fraction with ammonia and to find radioactivity which could not be assigned to these elements. The new activity appeared to follow thorium in many chemical steps. DEBIERNE gave the name actinium after the Greek word, Aktis, meaning ray, to this strange activity. His samples of actinium were, in fact, quite impure. GIESEL contributed greatly to the early studies of actinium. During the course of studies of pitchblende residues GIESEL isolated rare-earth fractions which had radioactive properties different from radium and polonium and, from what was known at the time, from DEBIERNE'S actinium. In particular, GIESEL noted that his preparations gave rise to an active gas (actinon) similar to radium emanation or thorium emanation but of much shorter period. Surfaces exposed to this emanation became strongly radioactive. GIESEL gave the name "emanium" or emanation body to the substance isolated with the rare earths which appeared to be the source of the radioactive gas. He withdrew this name when it later became evident that his "emanium" and DEBIERNE'S actinium were actually the same substance. GIESEL'S contribution was to show the close similarity of actinium to the rare earths rather than to thorium, as DEBIERNE had reported, and to call attention to the actinium emanation.

The rate at which actinium grows into pure $^{235}\text{U}$ or pure $^{231}\text{Pa}$ is shown in Figs. 6.36 and 6.37, respectively.

The Beta Decay of Actinium. The half-life of actinium is of considerable importance. For some years the value 13.5 year was accepted, but CURIE and BOUISSIERES reported a value of 21.7 year in 1944. Three subsequent investigations have given the values 22.0 year, 21.6 year, and 21.6 year, respectively, very close to CURIE and BOUISSIERES' value. The measurement of a half-life in this range requires a precise technique because the activity changes are slight within a convenient period of measurement (i.e., a few months to a year). The double ionization chamber method in which the ion current from one chamber is nearly balanced by the ion current from a second

---

Fig. 6.37. Growth of $^{227}$Ac into $^{231}$Pa.
chamber in which a long-lived radium sample of nearly equivalent activity is placed is well-suited for this purpose. A measurement by the coulometric technique\textsuperscript{190} gave a value of $21.2 \pm 0.8$ years in good agreement with the balanced chamber technique.

The end point of the beta spectrum of actinium was reported to be only 40 keV in an unpublished study by FRIEDMAN and CO-WORKERS.\textsuperscript{191} A careful study by BECKMANN and HUSTER\textsuperscript{192} showed an energy of $45.5 \pm 1.0$ keV with no evidence of a second component. NOVIKOVA and CO-WORKERS\textsuperscript{193} placed the end point between 42 and 45 keV. French authors\textsuperscript{194} reported the presence of 37 keV radiation in the beta decay of actinium but later\textsuperscript{195} showed that this radiation was actually fluorescent K x-radiation of lanthanum excited in the rare earth impurity in the sample by higher energy radiation. The most complete study of the gamma transitions was made by NOVIKOVA, VOLKOA, GOLDIN and TRETYAKOV\textsuperscript{193} who measured the M, N and O shell conversion electrons of gamma transitions with the energies $9.3 \pm 0.1$, $15.2 \pm 0.1$ and $24.5 \pm 0.2$ keV. From the conversion ratios in the M subshells it was concluded that all three transitions were mixed E\textsubscript{2} + M\textsubscript{1} in multipolarity, although the more energetic two were > 99 percent M\textsubscript{1}. The 9.3 and 15.2 keV transitions add to 24.5 so it is believed that they represent a cascade de-exciting a level at 24.5 keV. The gamma intensities imply a composite beta spectrum.

**The Alpha Branching of Ac\textsuperscript{227} and the Decay Properties of Actinium K.**

In 1914 MEYER, HESS and PANETH\textsuperscript{196} observed a group of low-intensity alpha particles in a pure actinium preparation in addition to alpha groups ascribed to unremoved traces of AcX. These new alpha particles of 3.56 cm range in air were ascribed to branch decay in Ac\textsuperscript{227}. This observation was subject to


\textsuperscript{192} W. Beckmann and E. Huster, Z. Naturf. 10a, 86 (1955); Z. Physik 142, 585 (1955).


\textsuperscript{194} Lecoin, Perey, Riou, Teillac, J. Phys. radium 11, 227 (1950).

\textsuperscript{195} Bouchez, Michalowicz, Riou and Teillac, J. Phys. radium 16, 344 (1955).

considerable doubt over the next two decades since it seemed possible that the new alpha particles could be ascribed to traces of protactinium or of actinium daughters. Mlle. PEREY\textsuperscript{197} settled the doubts conclusively in 1939 by chemically isolating from pure actinium preparation a 21 min. beta emitter which had the expected properties of the ekacesium isotope which the alpha decay of actinium should produce. The beta-emitting ekacesium was named Actinium K. PEREY established that the alpha branching in Ac\textsuperscript{227} was 1.2\%. Since AcK was the first isotope of element 87 ever to be established, Mme. PEREY is credited with the discovery of this element. For the name of the element, she chose francium (symbol Fr). The isotopes of francium are reviewed in Sec. 10.6 of Chapter 10 where it is shown that AcK is the longest-lived form of this element.

An energy of 4.942 MeV was reported\textsuperscript{198} for the alpha particles of Ac\textsuperscript{227} in 1952. These alpha particles were later given a careful restudy by NOVIKOVA, VOLKOVA, GOLDIN, ZIV and TRETYAKOV\textsuperscript{193} who found the complex spectrum summarized in Table 6.26. They also studied the conversion electrons emitted during the alpha decay of Ac\textsuperscript{227}. This study is difficult to carry out because of the low alpha branching and because of the electron lines contributed by daughter activities which grow into the sample. Most of the difficulties were circumvented by electron-alpha coincidence techniques. Evidence for transitions of the following energy was found: 12.7, 70.4, 84.5, 101, 166 and 190 keV. These gamma rays could be fitted naturally into the level scheme of Fr\textsuperscript{223} revealed by the alpha groups, as shown in Fig. 6.38.

These Russian authors discuss a possible interpretation of the Fr\textsuperscript{223} level scheme in terms of the collective model of the nucleus. According to this interpretation the levels at 0, 12.7, 166 and 193 keV are the $I = 3/2$, $1/2$, $7/2$ and $5/2$ members of a rotational band based on a $K = 1/2$ ground state assignment. This is an "anomalous" rotational band in which the $I$-spin ordering of the levels is reversed for the $1/2$, $3/2$ and $5/2$, $7/2$ pairs. NOVIKOVA ET AL. call attention to the fact that a similar set of levels occur in the nucleus, Fr\textsuperscript{221}. One interesting consequence of this interpretation is that it indicates that nuclei as light as 223 and 221 are deformed in the ground

\textsuperscript{197} M. Perey, J. Phys. radium (7) 10, 435 (1939); Compt rend. 208, 97 (1939).

Table 6.26 Alpha Spectrum of Ac$^{227}$
Novikova et al.$^{193}$

<table>
<thead>
<tr>
<th>Alpha group</th>
<th>Alpha Particle Energy (keV)</th>
<th>Energy of Daughter Level (keV)</th>
<th>Alpha Transition Intensity</th>
<th>Hindrance Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_0$</td>
<td>4949 ± 2</td>
<td>0</td>
<td>48.7 ± 3</td>
<td>67</td>
</tr>
<tr>
<td>$\alpha_{12}$</td>
<td>4936.5 ± 3</td>
<td>12.7</td>
<td>36.1 ± 3</td>
<td>8</td>
</tr>
<tr>
<td>$\alpha_{84}$</td>
<td>4866 ± 3</td>
<td>84.5</td>
<td>6.9 ± 1</td>
<td>14</td>
</tr>
<tr>
<td>$\alpha_{102}$</td>
<td>4849 ± 3</td>
<td>102</td>
<td>5.5 ± 1</td>
<td>14</td>
</tr>
<tr>
<td>$\alpha_{166}$</td>
<td>4786 ± 5</td>
<td>166</td>
<td>1.0 ± 0.5</td>
<td>40</td>
</tr>
<tr>
<td>$\alpha_{193}$</td>
<td>4759 ± 5</td>
<td>193</td>
<td>1.8 ± 0.5</td>
<td>17</td>
</tr>
<tr>
<td>$\alpha_{225}$</td>
<td>4728 ± 8</td>
<td>225</td>
<td>~0.1</td>
<td>---</td>
</tr>
<tr>
<td>$\alpha_{250}$</td>
<td>4704 ± 8</td>
<td>250</td>
<td>0.4 ± 0.2</td>
<td>38</td>
</tr>
<tr>
<td>$\alpha_{440}$</td>
<td>4516 ± 10</td>
<td>440</td>
<td>~0.2</td>
<td>---</td>
</tr>
</tbody>
</table>
Fig. 6.38. Decay scheme for the alpha branch decay of Ac$^{227}$ as formulated by Novikova et al.
state, at least if the mass number is odd.

We turn now to a discussion of the decay characteristics of actinium K. The endpoint energy of the beta particles of AcK is 1.2 MeV. The gamma rays have been studied by LECOIN ET AL. and by HYDE. In the work of the latter it was found that photons of a 49.8 keV gamma ray appear in 40% of the beta disintegrations and that photons of an 80 keV gamma ray appear in 24% of the disintegrations. Additional low-intensity gamma rays appear at 215- and 310-keV. A complete decay scheme has not been estabished.

From considerations of the systematics of alpha decay which are thoroughly discussed in Chapters 2 and 4, it was later deduced that AcK, which arises from a small alpha branching of Ac, must in turn show a small, but measureable, alpha branching. HYDE and GHIORSO established the correctness of this prediction by isolating the At daughter from a purified sample of AcK. Figure 6.39 summarizes their findings. The At daughter was isolated in an amount corresponding to an alpha branching of only $4 \times 10^{-5}$ in AcK. The At product has a half-life of 0.9 min. and shows an observable alpha branching of about 97% to produce the previously-unreported isotope, Bi. These experiments of HYDE and GHIORSO have the additional interest that they represent the first chemical isolation of astatine from a natural source. The alpha particle energy of AcK itself has been measured by photographic emulsion studies of freshly purified AcK samples by ADLOFF. He found a value of $5.34 \pm 0.08$ for the alpha particles of AcK and an alpha branching of $0.6 \times 10^{-4}$.

PEREY has published an excellent and authoritative short review of the physical and chemical properties of Actinium K.

Analysis of Actinium. Methods for the detection and analysis of actinium may be summarized as follows:

Fig. 6.39. Decay of actinium and its daughters showing branch products. The main path of the decay is shown in bold arrows. Actinium K and its rare branch products are shown at the left.
(1) **Measurement of total alpha activity.** The disintegration rate of a sample of pure actinium can be determined by measuring the total alpha activity of the daughters after these have come to equilibrium. Alternatively one can measure the growth of the alpha activity over the first few weeks and compare this with the theoretical growth curve of Fig. 6.40. Any extraneous alpha activity such as ionium impurity will give an erroneous result. It is therefore desirable to check the identity of the daughter alpha activity by alpha spectrum analysis using an ionization chamber or solid state detector coupled to a pulse-height analyzer.

(2) **Measurement of total beta activity.** Two beta-emitters appear in the decay chain of actinium; these are AcB and AcC". When actinium comes to equilibrium with its daughters a measurement of the beta radiation indicates the amount of actinium. This growth of hard beta radiation into purified actinium is shown by Curve D of Fig. 6.40. The sample is usually covered to prevent the escape of actinon. Some absorber must be placed over the sample to filter out the alpha particles when thin window beta-counters are used. Any beta-emitting impurities in the sample will cause erroneous results. A modification of this method 203 consists of the chemical isolation of AcB (Pb211) by coprecipitation with added lead carrier precipitated as lead sulfide. The radioactivity of the 36 minute AcB in equilibrium with its AcC daughter is then followed in a suitably calibrated counter. This method is very sensitive and can be applied to samples containing as little as 10^{-2} microcuries of actinium provided the actinium is in equilibrium with all its descendents. This method can be applied to an actinium sample diluted with inert rare earth or other contaminants. Also, the actinium sample can be contaminated with beta emitting nuclides provided they do not coprecipitate with lead sulfide from acid solution. It cannot be applied to actinium samples contaminated with radium or thorium.

(3) **Measurement of total gamma activity.** When the source strength is of the order of a millicurie or greater a suitable method of measure-

---

Fig. 6.40. Growth of alpha activity of 18.17 day radioactinium (Th\textsuperscript{227}) (Curve A) and 11.68 day actinium -X (Ra\textsuperscript{223}) (Curve B) into pure actinium. Curve C is the total alpha activity in the sample and includes contributions from the short-lived descendents actinon (3.92 sec Em\textsuperscript{219}), actinium-A (1.83 x 10\textsuperscript{-3} sec Po\textsuperscript{215}), and actinium-C (2.16 m Bi\textsuperscript{211}) which are in equilibrium with the actinium-X. Curve C is based on the assumption that no actinon is lost. Growth of hard beta activity into actinium (Curve D); this curve represents the activity of AcB (36.1 m Po\textsuperscript{211}) and AcC (4.79 m Tl\textsuperscript{207}) whose growth into pure actinium is controlled by the growth of AcX.
The determination of the gamma activity of the equilibrium mixture of activities. The sample is sealed in a glass tube and lead absorbers 1 cm in thickness are used to cut out beta particles and low-energy gamma rays. The gamma activity registered in an ion chamber can be compared to a standard radium sample. This determination can be made to an accuracy of about 3% and sample size can be as low as 1 microcurie. The sensitivity of this method can be raised by use of an end-window counter to measure the radiations emitted from a standard volume of solution containing actinium in equilibrium with its descendents. Samples as small as 0.003 microcuries can be assayed. No chemical operations are necessary.

(4) Calorimetric measurement. The amount of actinium in a sample can be determined by direct measurement of the heat liberated by a source in a calorimeter. The principal energy is derived from absorption of the alpha particles and the alpha-recoil products. The energy of each successive alpha disintegration can be accurately calculated taking into account branching and complex structure. (See Table 6.8 in radium section.) The partial absorption of beta and gamma radiations contributes 10% as much energy as do the alpha particles plus recoils. From the inner wall thickness of the calorimeter and the absorption curve of the beta-gamma radiation, one can calculated the total heat liberated per hour by a curie of actinium. The calorimetric measurement can be made with an accuracy of 1 to 2%.

(5) Separation and measurement of actinon. A sensitive test for the presence of actinium or of radioactinium or of actinium-X in a radioactive sample is the removal of the gaseous emanation, actinon, from the sample. The actinon may be swept from a solution in a stream of air and carried directly into a counter. It is also possible to collect the active deposit from the air stream on a negatively-charged plate and count it separately. The actinon method does not lend itself

to an accurate analysis because of the 3.92 sec. half-life of actinon but it serves as a very sensitive method of detection. In the case of recently purified actinium it is necessary to wait until RdAc and AcX have grown into the sample before actinon is found.

(6) Separation of actinium-X and the measurement of its activity by subsequent separation and counting of actinium-B. In this method, actinium-X is separated by coprecipitation on barium sulfate. The sulfate is converted to the carbonate and then to the soluble chloride. When the separated actinium-X is again in solution its daughter product actinium-B, the 36 minute Pu211 isotope, is removed by coprecipitation on lead sulfide and the beta decay of AcB and its short-lived AcC daughter are followed in a suitably calibrated counter. With a slight modification this can be applied to samples contaminated with the radium or the thorium series activities. It can be applied to insoluble or partially soluble solid samples and is particularly suited to the assay of actiniferous minerals. In the case of insoluble samples such as minerals, a fusion with the bisulfate of potassium in the presence of 100 milligrams of barium chloride is carried out. The barium sulfate formed in this step removes the actinium-X, plus all other isotopes of radium, lead or bismuth in the sample. The barium sulfate is metathesized successively to the carbonate and the chloride. The chloride is put into solution and emanation isotopes are removed by boiling. A scavenger precipitate of lead sulfide removes a mixture of the lead and bismuth activities of all three natural radioactive series. The activities constituting the active deposit of the actinium series re-establish equilibrium much more quickly than the corresponding activities in the decay chains of radium and thorium. Hence a second lead sulfide precipitate removed 30 minutes later will carry down only AcB.

(7) By isolation of AcK daughter product. Methods (1) through (6) depend upon the growth of 18.17 day RdAc and 11.68 day AcX into the actinium and hence all suffer from the serious disadvantage that many weeks must elapse before an accurate analysis is possible. There are

two alternative methods to which this disadvantage does not apply.

One of these is discussed in (8) below. The other method is based on the isolation and measurement of AcK (Fr$^{223}$), the alpha decay branch product of Ac$^{227}$. As discussed above, Ac$^{227}$ undergoes alpha decay in 1.2% of its disintegrations. The alpha-decay product is the 21 min. beta emitter AcK which comes to equilibrium with Ac$^{227}$ within two hours. Perey, 209 who proposed this rapid method, recommended the following procedure:

Sodium carbonate is added to the actinium solution to precipitate actinium and rare earths leaving AcK in solution. Barium chromate is then precipitated to remove AcX and AcC and lanthanum hydroxide is precipitated to carry out any traces of actinium which may remain. The filtered solution is then evaporated rapidly to dryness and the beta activity is measured. From the decay curve of the 21 min. activity the amount of AcK present at the time of removal of the carbonate precipitate is determined by back-extrapolation. From this the amount of actinium can be calculated after allowing for the alpha branching of 1.2%. With suitable counting techniques the range of applicability of this method is 1 microgram to 100 millicuries of actinium.

Hyde 210 has proposed a modified version of the AcK procedure based on the coprecipitation of AcK on free silicotungstic acid (which is insoluble in concentrated hydrochloric acid.)

(8) *By measurement of alpha particles of Ac$^{227}$. If a sample of Ac$^{227}$ is thoroughly decontaminated from all daughter activity and then immediately inserted in an alpha counter the observed alpha activity corresponds to the 1.2% alpha branching of Ac$^{227}$. To insure that the alpha particles detected are in fact due to Ac$^{227}$ and not to unseparated daughter activity (RdAc being the most difficult to separate) it


is desirable to submit the sample to alpha spectrum analysis using an ionization chamber (or solid state detector) and pulse-height analysis. PEPPARD$^{211}$ has discussed this method of actinium assay. It has also been studied by GLOVER, BEADLE and ROGERS$^{212}$ who report that with proper sample preparation and proper analysis of the alpha spectrum the Ac$^{227}$ alpha particles can be measured even in the presence of unseparated daughter activity.

Artificial Synthesis of Actinium. In modern times the availability of high neutron fluxes in nuclear reactors has made it possible to synthesize weighable quantities of Ac$^{227}$ by means of the reactions:

$$Ra^{226} (n,\gamma) Ra^{227} \rightarrow Ra^{227} \rightarrow Ac^{227}$$

$$\sigma = 15 \text{ barns}$$

PETERSON$^{213}$ in 1945 first demonstrated this synthesis by irradiation of 1 milligram of radium. Later HAGEMANN$^{214}$ irradiated a series of one gram samples of radium and isolated milligram quantities of actinium. This was the first isolation of chemically-pure actinium on the milligram scale; previous to this, the best preparations of actinium contained only a few percent of actinium. The synthetic approach has two pronounced advantages: (1) the material which needs to be isolated from radioactive ores is radium which occurs in much higher concentration and is relatively easy to obtain in the pure state, and (2) contamination with the difficultly-separable rare earths is completely avoided.

Radioactinium (Th$^{227}$). The immediate decay product of the beta decay of Ac$^{227}$ is Th$^{227}$ which is an alpha emitter with a half-life of 18.17 days.$^{215}$ This isotope, also called radioactinium, has been the subject of considerable

interest because of the extraordinary complexity of its alpha and gamma spectra. A detailed account of these radiations is given in Sec. 8.2.5 of Chapter 8.

By standard radiochemical methods radiothorium can easily be separated from its actinium parent and from its daughter products. Its immediate daughter, actinium-X, has a half-life of 11.68 days so that contaminating daughter-product activity grows in only at a moderate rate. This growth is shown quantitatively in Fig. 6.41. The growth of radioactinium into an initially pure sample of actinium is shown in Fig. 6.40.

Actinium-X (Ra$_{223}$). The independent discovery of actinium-X by Godlewski (1905) and Giesel (1904) is mentioned in the historical introduction, Sec. 6.1. This nuclide is an alpha emitter whose half-life has recently been redetermined as $11.68 \pm 0.06$ days$^{216}$ and as $11.22 \pm 0.05$ days$^{215}$. It can be separated from actinium or from radioactinium after a suitable growth period, which can be determined from Fig. 6.40 or 6.41. Samples of actinium-X are never pure from the radioactivity standpoint because actinon and AcA daughters re-establish their equilibrium value within a minute of the purification of actinium-X. The longest-lived daughter is AcB (Pb$_{211}$) but even this product comes to equilibrium within a few hours. Figure 6.42 shows the growth of daughters into actinium-X.

Actinium-X is an alpha emitter resembling its parent, radioactinium, in the complexity of its alpha and gamma ray spectrum. ROSENBLUM, PEREY, VALADARES and GUILLOT$^{217}$, ASARO$^{218}$, PILGER$^{219}$, RYTZ$^{219a}$ and WALEN, NEDOVESOV and BASTIN-SCOFFIER$^{227b}$ have studied the alpha spectrum of AcX.

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217. Rosenblum, Perey, Valadares and Guillot, as quoted by Hollander, Perlman and Seaborg in Rev. Mod. Phys. 25, 600 (1953).
Fig. 6.41. Curve A - regrowth of 11.68 day AcX (Ra$^{223}$) alpha activity into purified 18.17 day RdAc (Th$^{227}$). Curve B - decay of alpha activity of RdAc. Curve C - total alpha activity in initially pure RdAc sample including contributions from RdAc, AcX, actinon, AcA and AcC.
Fig. 6.42. Variation with time of total alpha activity in an initially pure sample of 11.7 day AcX (Ra\textsuperscript{223}). Curve A shows AcX itself. After a few seconds, Curve A also represents 3.92 sec. actinon (Em\textsuperscript{219}) and 0.00183 sec. AcA (Po\textsuperscript{215}). Curve B shows 36.1 min. beta-emitter AcB (Po\textsuperscript{211}). Curve C represents 2.16 min. AcC (Bi\textsuperscript{211}) which is an alpha emitter. Curve D is the total alpha activity including AcX, An, AcA, and AcC. When transient equilibrium is reached all activities decay with the controlling half-life of 11.7 days.
The gamma and conversion electron spectra have been measured by several groups, and partial decay schemes have been constructed by several authors. The study of PILGER'S was particularly thorough in its experimental analysis of the alpha spectrum, the gamma spectrum and the conversion electron spectrum and we quote here the principal findings of his report. He studied the alpha spectrum in a homogeneous-field magnetic spectrograph of high resolution and also in a double-focusing magnetic spectrometer of high resolution and transmission and obtained the results summarized in Table 6.27. With a sodium iodide crystal spectrometer he was able to resolve a few of the prominent gamma rays from the complex gamma spectrum in spite of serious interference from the gamma radiation of the daughter products. He performed some gamma-gamma coincidence studies. More significantly, he was able to employ the double-focusing alpha spectrometer in an alpha-gamma coincidence arrangement in which the gamma spectrum in coincidence with alpha particles of a particular energy could be measured. This coincidence technique is a very powerful method for testing the placement of gamma rays in the decay scheme of an alpha emitter. The results are summarized in Table 6.28. The angular correlation of the 270 keV photons with respect to the alpha particles leading to the 270 keV level in the daughter nucleus was measured and shown to agree with the spin and multipolarity assignments of the proposed decay scheme.

PILGER found some difficulty in studying the conversion electrons of AcX in a standard permanent-magnet electron spectrograph because the actinon diffused out of the necessarily-thin source plate, spread throughout the spectrograph chamber, and fogged the emulsion. This difficulty was not so marked in his double-focusing variable-field beta spectrometer and he was able to measure many of the conversion electrons from the numerous gamma transitions.

Table 6.27 Alpha Groups of Ra\textsuperscript{223}

<table>
<thead>
<tr>
<th>Energy (MeV)</th>
<th>Intensity (%)</th>
<th>Energy of Daughter State (keV)</th>
<th>Log Hindrance Factor</th>
<th>Energy (MeV)</th>
<th>Intensity (%)</th>
<th>Energy of Daughter State (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.8696</td>
<td>0.87</td>
<td>0</td>
<td>3.46</td>
<td>5.870</td>
<td>0.96</td>
<td>0</td>
</tr>
<tr>
<td>5.8654</td>
<td>&lt;.02</td>
<td>[4.3]</td>
<td>&gt;5.1</td>
<td>5.865?</td>
<td>[4.8]</td>
<td></td>
</tr>
<tr>
<td>5.8555</td>
<td>0.32</td>
<td>14.35</td>
<td>3.82</td>
<td>5.856</td>
<td>0.3</td>
<td>14.4</td>
</tr>
<tr>
<td>5.7454\textsuperscript{b}</td>
<td>9.1</td>
<td>126.4</td>
<td>1.84</td>
<td>5.745</td>
<td>10.5</td>
<td>127.0</td>
</tr>
<tr>
<td>5.7141\textsuperscript{b}</td>
<td>53.7</td>
<td>158.3</td>
<td>0.91</td>
<td>5.715</td>
<td>50.4</td>
<td>158.9</td>
</tr>
<tr>
<td>5.6051\textsuperscript{b}</td>
<td>26</td>
<td>269.3</td>
<td>0.67</td>
<td>5.605</td>
<td>23.6</td>
<td>(269.6)</td>
</tr>
<tr>
<td>5.5376\textsuperscript{b}</td>
<td>9.1</td>
<td>338.1</td>
<td>0.77</td>
<td>5.537</td>
<td>10.3</td>
<td>338.5</td>
</tr>
<tr>
<td>5.4996</td>
<td>0.8</td>
<td>378.9</td>
<td>1.63</td>
<td>5.500</td>
<td>0.86</td>
<td>376.5</td>
</tr>
<tr>
<td>5.4792</td>
<td>~8x10\textsuperscript{-3}</td>
<td>397.5</td>
<td>3.51</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.4316</td>
<td>2.3</td>
<td>446</td>
<td>0.80</td>
<td>5.432</td>
<td>2.4</td>
<td>445.6</td>
</tr>
<tr>
<td>5.3636</td>
<td>0.11</td>
<td>515</td>
<td>1.80</td>
<td>5.363</td>
<td>0.20</td>
<td>515.6</td>
</tr>
<tr>
<td>5.3367</td>
<td>0.10</td>
<td>542.6</td>
<td>1.64</td>
<td>5.337</td>
<td>0.07</td>
<td>541.8</td>
</tr>
<tr>
<td>5.2853</td>
<td>0.13</td>
<td>595</td>
<td>1.24</td>
<td>5.282</td>
<td>0.3</td>
<td>589.6</td>
</tr>
<tr>
<td>5.2808</td>
<td>0.095</td>
<td>600</td>
<td>1.33</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>5.2568</td>
<td>0.043</td>
<td>624</td>
<td>1.55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.2343</td>
<td>0.042</td>
<td>647</td>
<td>1.43</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>5.2096</td>
<td>0.0054</td>
<td>672</td>
<td>2.18</td>
<td></td>
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<td>5.1708</td>
<td>0.026</td>
<td>712</td>
<td>1.27</td>
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<td></td>
</tr>
<tr>
<td>5.1498</td>
<td>0.021</td>
<td>733</td>
<td>1.24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.1328</td>
<td>~1.7x10\textsuperscript{-3}</td>
<td>748</td>
<td>2.24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.1104</td>
<td>~6 x10\textsuperscript{-4}</td>
<td>773</td>
<td>2.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0842</td>
<td>~3 x10\textsuperscript{-4}</td>
<td>800</td>
<td>2.71</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0540</td>
<td>~2 x10\textsuperscript{-4}</td>
<td>830</td>
<td>2.69</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0340</td>
<td>~4 x10\textsuperscript{-4}</td>
<td>851</td>
<td>2.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0235</td>
<td>~6 x10\textsuperscript{-4}</td>
<td>861</td>
<td>1.99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0124</td>
<td>~4 x10\textsuperscript{-4}</td>
<td>873</td>
<td>2.07</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Pilger's energy values were recalculated on the basis of the energy standards used by Walen et al.

\textsuperscript{b}Rytz gives the values 5.7455, 5.7143, 5.6053 and 5.5371 MeV, respectively, for the four main groups.
Table 6.28 Summary of Ra$^{223}$ $\alpha$-$\gamma$ Coincidence Study

<table>
<thead>
<tr>
<th>Alpha Group</th>
<th>Observed Radiation (keV)</th>
<th>Intensity$^1$ photons/alpha</th>
<th>$\alpha$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{127}$</td>
<td>K x-ray</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>122</td>
<td>0.19</td>
<td>3.6</td>
</tr>
<tr>
<td>$\alpha_{158}$</td>
<td>K</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>144</td>
<td>0.082</td>
<td></td>
</tr>
<tr>
<td></td>
<td>154</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>$\alpha_{270}$</td>
<td>K</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>0.43</td>
<td>0.95</td>
</tr>
<tr>
<td>$\alpha_{338}$</td>
<td>K</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>145-155</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>0.017</td>
<td></td>
</tr>
<tr>
<td></td>
<td>338</td>
<td>0.49</td>
<td>0.33</td>
</tr>
<tr>
<td>$\alpha_{376}$</td>
<td>K</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>376</td>
<td>0.45</td>
<td>0.71</td>
</tr>
<tr>
<td>$\alpha_{445}$</td>
<td>K</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>445</td>
<td>0.48</td>
<td>0.71$^2$</td>
</tr>
</tbody>
</table>

$^1$ K x-ray intensity in vacancies/alpha; i.e., the Auger effect correction has been made.

$^2$ A possible cascade was not distinguished with certainty from Compton distribution and backscatter peak.
in the decay of AcX. His deductions on the energies, intensities and multipolarities of the gamma transitions are summarized in Table 6.29.

From consideration of all his data, PILGER was able to formulate the principal features of the decay scheme of Ra$^{223}$ with reasonable certainty and to draw the decay scheme shown in Fig. 6.43. Our knowledge of the intrinsic quantum states and of collective modes of excitation are in an elementary and developing stage for nuclei in this range of atomic masses so that no detailed interpretation of this decay scheme is given.

Later work by WALEN, NEDOVESOV and BASTIN-SCOFFIER$^{227b}$ on the alpha spectrum showed 14 additional low-intensity groups beyond those observed by Pilger. These are listed in Table 6.27. Drawing on their own results and on some results of BRAGANÇA-GIL$^{226a}$ and of PETIT$^{226a}$ these authors draw tentative conclusions about the intrinsic and collective nature of several of the An$^{219}$ levels; because of the necessarily-tentative nature of these conclusions we do not reproduce them here.

Actinon. The gaseous emanation in the actinium series is the 3.92 second nuclide, An$^{219}$. The alpha spectrum of actinon has been investigated in magnetic spectrographs by ROSENBLUM, GUILLOT and PEREY$^{227}$ by PILGER$^{219}$ by RYTZ$^{219a}$ and by WALEN, NEDOVESOV and BASTIN-SCOFFIER$^{227b}$ with results shown in Table 6.30. PILGER did not observe the group at 6.197 MeV reported by ROSENBLUM ET AL.

There is difficulty in the precise measurement of the alpha energies of Em$^{219}$. Because of the short half-life the spectrum has to be studied in samples of Ra$^{223}$ with which the emanation is in equilibrium. Since the product nuclei recoil with considerable kinetic energy after alpha emission they are expelled from the source plate or imbedded in it. Those expelled are no longer in focus in the spectrograph; the alpha spectrum obtained from those remaining in the plate shows significant line-broadening due to energy loss in the mass of source plate covering the now-imbedded atoms of daughter activity.

Gamma rays of 270 and 400 keV have been observed by sodium iodide crystal spectrometer examination of gaseous actinon and the conversion electrons of these same transitions of actinon were observed by PILGER$^{219}$ in

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Fig. 6.43. Decay scheme of AcX (Ra\textsuperscript{223}). After Pilger\textsuperscript{219} This figure does not show the 13 low intensity alpha transitions to An levels above 595 keV reported by Walen et al.\textsuperscript{227b}
Table 6.29 Internal Transitions in Decay of Ra$^{223}$

<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>Intensity (%)</th>
<th>Multipolarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.2</td>
<td>1.4</td>
<td>M1</td>
</tr>
<tr>
<td>68.4</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>122.2</td>
<td>11</td>
<td>M1-E2</td>
</tr>
<tr>
<td>143.0</td>
<td>~1</td>
<td>(M1 ?)</td>
</tr>
<tr>
<td>144.1</td>
<td>19</td>
<td>M1 (Some E2?)</td>
</tr>
<tr>
<td>154.1</td>
<td>28</td>
<td>M1</td>
</tr>
<tr>
<td>158.3</td>
<td>3.2</td>
<td>M1</td>
</tr>
<tr>
<td>179.6</td>
<td>1.1</td>
<td>M1</td>
</tr>
<tr>
<td>269.6</td>
<td>21.4</td>
<td>M1</td>
</tr>
<tr>
<td>323.8</td>
<td>4.9</td>
<td>M1</td>
</tr>
<tr>
<td>338.0</td>
<td>4.2</td>
<td>M1</td>
</tr>
<tr>
<td>371.1</td>
<td>0.7</td>
<td>M2</td>
</tr>
<tr>
<td>440.6</td>
<td>0.6</td>
<td>M2</td>
</tr>
<tr>
<td>445.6</td>
<td>1.4</td>
<td>M2</td>
</tr>
<tr>
<td>580.4</td>
<td>~0.4</td>
<td></td>
</tr>
</tbody>
</table>
Table 6.30 Alpha Groups of Actinon

<table>
<thead>
<tr>
<th>Group</th>
<th>Particle Energy (MeV)</th>
<th>Abundance (%)</th>
<th>Excited State Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rosenblum</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_0$</td>
<td>6.807$^a$</td>
<td>69</td>
<td>(0)</td>
</tr>
<tr>
<td>$\alpha_{270}$</td>
<td>6.542</td>
<td>15</td>
<td>270</td>
</tr>
<tr>
<td>$\alpha_{397}$</td>
<td>6.417</td>
<td>12</td>
<td>397</td>
</tr>
<tr>
<td>$\alpha_{622}$</td>
<td>6.197</td>
<td>4</td>
<td>622</td>
</tr>
<tr>
<td><strong>Pilger</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_0$</td>
<td>6.813 ± 0.002$^b$</td>
<td>82</td>
<td>(0)</td>
</tr>
<tr>
<td>$\alpha_{271}$</td>
<td>6.547</td>
<td>13</td>
<td>271.6</td>
</tr>
<tr>
<td>$\alpha_{401}$</td>
<td>6.419</td>
<td>5</td>
<td>401</td>
</tr>
<tr>
<td><strong>Rytz</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_0$</td>
<td>6.8176 ± 0.0010$^c$</td>
<td></td>
<td>(0)</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>6.5509</td>
<td>11.5</td>
<td>271.6</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>6.4239</td>
<td></td>
<td>401</td>
</tr>
<tr>
<td><strong>Walen, Nedovessov, and Bastin-Scoffier</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_0$</td>
<td>6.8175</td>
<td>81</td>
<td>0</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>6.5513</td>
<td>11.5</td>
<td>271.2</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>6.5275</td>
<td>0.12</td>
<td>295</td>
</tr>
<tr>
<td>$\alpha_3$</td>
<td>6.4232</td>
<td>7.5</td>
<td>401.6</td>
</tr>
<tr>
<td>$\alpha_4$</td>
<td>6.3103</td>
<td>0.094</td>
<td>516.6</td>
</tr>
<tr>
<td>$\alpha_5$</td>
<td>6.2221</td>
<td>2.6 x 10^{-3}</td>
<td>606.4</td>
</tr>
<tr>
<td>$\alpha_6$</td>
<td>6.1571</td>
<td>1.74 x 10^{-2}</td>
<td>672.6</td>
</tr>
<tr>
<td>$\alpha_7$</td>
<td>~6.1462</td>
<td>~2.6 x 10^{-3}</td>
<td>683.7</td>
</tr>
<tr>
<td>$\alpha_8$</td>
<td>6.1005</td>
<td>3 x 10^{-3}</td>
<td>730.3</td>
</tr>
<tr>
<td>$\alpha_9$</td>
<td>5.9993</td>
<td>4.4 x 10^{-3}</td>
<td>833.4</td>
</tr>
</tbody>
</table>

$^a$Recalculated by BRIGGS.
$^b$Relative to $\alpha_0$ of Cm$^{242}$ taken as 6.110 MeV.
$^c$Relative to Po$^{210}$ $E_\alpha = 5.3048$. 
his study of Ra$^{223}$ samples. BRAGANCA-GIL and PETIT$^{227c}$ have also investigated the decay of An$^{219}$ by alpha-gamma coincidence techniques.

Actinium-A (Po$^{215}$). AcA (Po$^{215}$) decays with a half-life of 0.00183 seconds. It emits alpha particles the energy of which have been given as 7.38 MeV,$^{227a}$ 7.36 MeV$^{219}$ and 7.384 MeV.$^{219a}$ Two additional alpha groups of very low intensity have been reported,$^{227c}$ 6.954 MeV($\sim 3.4 \times 10^{-2}\%$) and 6.948 MeV($\sim 2.2 \times 10^{-2}\%$).

Some evidence for a possible $\beta^-$ branching of AcA to produce At$^{215}$ has been presented. KARLIK and BERNERT$^{228}$ examined the alpha activity in a weak sample of the 3.92 second actinon activity from the U$^{235}$ series and found a small number of previously unreported 8.4 MeV alpha-particles. These were ascribed to an extremely short-lived At$^{215}$ resulting from a $5 \times 10^{-4}\%$ $\beta^-$ branching in AcA. As originally reported these results were open to objections on energetic grounds as discussed by FEA HER.$^{229}$ The work was repeated by AVIGNON$^{230}$ in France on a considerably larger sample with substantially the same results except that the alpha-particle energy was determined to be 8.04 MeV. This revision of the alpha-energy removes one main objection to the assignment, (i.e., the non-equivalence of the AcA - At$^{215}$ - AcC energy sum and the AcA - AcB - AcC energy sum) and makes it possible to identify this At$^{215}$ with the At$^{215}$ discovered by MEINKE$^{231}$ in the Pa$^{227}$ collateral series produced by cyclotron bombardments. Nevertheless, more conclusive evidence is desirable on this question.

The Active Deposit of Actinon. The gas, actinon, deposits an invisible film of radioactive daughter products upon any surface exposed to it and by collection of the charged daughter products on an electrically-charged wire or surface the deposit can be highly localized. Since the immediate

228. B. Karlik and T. Bernert, Z. Physik 123, 51 (1944); Naturwissenschaften 32, 44 (1943).
229. N. Feather, Nucleons 5, 22 (1949).
daughter product of actinon is the 0.00183 second AcA. The active deposit of actinon is normally considered to consist of AcB and its daughter products which are listed in Table 6.31. The decay schemes and genetic relationships of the members of the active deposit of actinon are displayed in Fig. 6.44. The activity changes in a sample of active deposit as a function of time are plotted in Fig. 6.45.

Rather pure samples of AcC can be obtained by the simple technique of heating the plate on which the active deposit is located, since bismuth is less volatile than lead or thallium. AcB, AcC or AcC" can also be prepared in a pure state by electrodeposition or by chemical separation methods.

AcC undergoes branching decay in 0.32% of its disintegrations to produce AcC' (Po211). For many years the value of the half-life of Po211 was listed as 5 x 10^-3 seconds. This value had not been obtained experimentally, but by an estimate based on the Geiger-Nuttall energy-versus-half-life relationship, which unfortunately, gives erroneous results for the low-mass polonium isotopes. LEINIGHER, SEGRE and SPIESS232,233 determined this half-life experimentally and obtained a value of 0.52 seconds.

It has been shown by experiments of artificial transmutation that Po211 exists in two isomeric forms. The ground state is the 0.52-second alpha emitter which appears as AcC' in the active deposit of the actinium series, as the electron capture decay product of the artificially prepared isotope At211, and as the alpha decay product of Em215, also an artificially prepared isotope. SPIESS233 found that helium ion bombardment of Po208 produces the 0.52-second Po211, and in addition, a 25-second isomeric form emitting 7.14 MeV alpha particles. JENTSCHKE and CO-WORKERS234 and PERLMAN and CO-WORKERS234a extended this investigation and constructed the decay scheme shown in Fig. 6.46. This is one of the most unusual cases of isomerism known. The failure to see any transition from the 25-second level in Po211 to the 0.52-second level means that these two levels differing in energy by 1.27 MeV

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232. R.F. Leininger, E. Segre, and F.N. Spiess, Phys. Rev. 82, 334A (1951); See also Spiess.233
Fig. 6.44. Decay scheme of the active deposit of actinon. Energies of levels and Q values are given in MeV. Intensities of gamma rays in the decay of AcB to AcC are given in percent by numbers at the tips of the arrows. Intensities of $\beta$ and $\alpha$ transitions are given in percent.
Fig. 6.45. Activity changes in actinon active deposit. Curve A shows decay of AcB beta activity or AcC alpha activity for a sample of active deposit prepared by a long exposure to actinon. Curve B shows growth of AcC alpha activity into an initially-pure sample of AcB prepared by a short exposure to actinon. Curve C illustrates the growth of AcC' beta activity into a sample of active deposit prepared by a short exposure to actinon.
Fig. 6.46. Decay schemes of the Po$^{211}$ isomers and of Bi$^{207}$. 
Table 6.31 The Actinium Series Active Deposit

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Type of Radiation</th>
<th>Energy and Abundance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>AcB (Pb$^{211}$)</td>
<td>β$^-$</td>
<td>1.39 MeV (~80%) ~0.5 (20%)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>γ</td>
<td>0.065, 0.083, 0.404, 0.425</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.487, 0.764, 0.829</td>
<td></td>
</tr>
<tr>
<td>AcC (Bi$^{211}$)</td>
<td>β$^-$</td>
<td>6.617 (83%) 6.273 (17%)</td>
<td>3, 4, 5, 6, 11, 12</td>
</tr>
<tr>
<td></td>
<td>γ</td>
<td>Energy unknown $\gamma_{\beta^-} = 0.61$ calc.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>α 0.32%</td>
<td>0.351 mJ (with alpha branch)</td>
<td>1, 3, 13</td>
</tr>
<tr>
<td></td>
<td>α 99.68%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>β</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acc' (Po$^{211}$)</td>
<td>α</td>
<td>7.434 (99%) 6.895 (0.50%)</td>
<td>7, 8, 9, 10</td>
</tr>
<tr>
<td></td>
<td>γ</td>
<td>0.562, 0.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>γ 0.52 sec.</td>
<td>1.47</td>
<td>1</td>
</tr>
<tr>
<td>Acc'' (Tl$^{207}$)</td>
<td>β</td>
<td>0.870 (~0.5%)</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>α 99.54%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>β</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AcD (Pb$^{207}$)</td>
<td>Stable</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4. M.G. Holloway and M.S. Livingston, Phys. Rev. 54, 18 (1938); Summarizes work of various investigators.
must have a spin difference of 5 or more.

The shell model provides a reasonable explanation for this decay scheme. The levels of Pb\(^{207}\) are known quite well from a study of the decay of Bi\(^{207}\) (see Chapter 10) and the spin and parity assignments correspond to those expected of a nucleus with one neutron less than a closed shell of 126. These single particle (hole) assignments are given in Fig. 6.46. The ground state of Po\(^{211}\) (the 0.52-second isomer) may be expected to have the spin value \(9/2\) resulting from a configuration with two protons beyond Pb\(^{208}\) as \((h_{9/2})^2\) paired to a resultant \(J = 0\) and an odd neutron as \(g_{9/2}\). The 25-second isomer of Po\(^{211}\) must have a spin \(\geq 19/2\) according to the arguments advanced by JENTSCHKE, JUVELAND and KINSEY. One cannot account for a spin value of this magnitude by the angular momentum of the odd neutron alone. It is necessary to consider the excitation of the 2 protons as well as the single neutron beyond the Pb\(^{208}\) core. When this possibility is included it is possible to write down several configurations of the available shell-model states which couple to a total angular momentum greater than 19/2.

MANG\(^{235}\) has made a highly interesting theoretical study of the alpha decay of the 0.52-second isomer of Po\(^{211}\). The usual one-body treatment of alpha decay contains an unrealistic assumption of a preformed alpha particle moving freely within the nuclear interior and prevented from escape only by the potential barrier at the nuclear edge. MANG\(^{235}\) replaced this picture with a much more realistic model in which the particles within the nucleus are considered as individual shell model particles. Alpha emission is presumed to occur when the wave functions of 2 neutrons and 2 protons overlap at the nuclear edge within a nuclear volume corresponding to the dimensions of an alpha particle. By inserting into his theoretical equations shell model oscillator wave functions chosen to agree with experimental Po\(^{207}\) energy levels and spin assignments, MANG was able to predict a correct value for the alpha decay constant and for the relative intensities to the ground, and the first two excited states of Po\(^{207}\). He was also able to specify the mixture of alpha waves of various angular momentum values leading to the excited states. The agreement of theoretical and experimental values for these quantities is

excellent. MANG assigned to $^{211}\text{Po}$ the configuration

$$\begin{pmatrix} h_9/2 \otimes \epsilon_{9/2} \end{pmatrix}_{I = 25/2}$$

Actinium-D. The stable end-product of the actinium series is $^{207}\text{Po}$ known as AcD or actinium-lead. AcD has undetectable alpha activity. Lead of mass 207 was first found by ASTON in lead isolated from a uranium mineral. RUTHERFORD concluded from the high ratio of $^{207}\text{Pb}$ to $^{208}\text{Pb}$ that $^{207}\text{Pb}$ must be identical with actinium-lead. This observation helped to clear up some of the confusion surrounding the origin of the actinium series and of the mass numbers of the members of the series.

The ratio of $^{207}\text{Pb}$ to $^{235}\text{U}$ in a uranium mineral which contains no primary lead and which has remained unaltered since its formation is a direct measure of the age of the mineral through straightforward application of the laws of radioactive decay. Another widely used dating method is the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio method. These methods are described in the following main section of this chapter.

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General Classification of Lead Samples. Any sample of terrestrial lead consists of a mixture of the four stable isotopes; Pb\(^{204}\), Pb\(^{206}\), Pb\(^{207}\) and Pb\(^{208}\). Lead differs from the great majority of elements in that the proportions of the various isotopes vary markedly from sample to sample. This result can be attributed to the steady production of the isotopes Pb\(^{206}\) (RaG), Pb\(^{207}\) (AcD) and Pb\(^{208}\) (ThD) from the decay of uranium and thorium widely distributed in the rocks of the earth's crust. Several types of lead mixtures have been distinguished:

Primeval (or primordial or original) lead is that mixture of lead isotopes which existed at the time of the completion of the element forming process which produced the matter of which the solar system is composed. It is not known with certainty what this isotopic mixture was. One can set upper limits to the contents of Pb\(^{206}\), Pb\(^{207}\) and Pb\(^{208}\) in primordial lead by analyzing many lead samples with particular attention to samples with a high content of Pb\(^{204}\). Since Pb\(^{204}\) is not formed in any decay process occurring in the natural radioactivities, primeval lead must have a Pb\(^{204}\) content at least as great as that of any single analyzed sample. Among many hundreds of terrestrial lead samples, one taken from the Rosetta Mine, South Africa, has shown the highest content of Pb\(^{204}\), the complete analysis being given in Table 6.32. In 1953 an important paper by Patterson, Brown, Tilton and Inghram\(^{236}\) reported an analysis of meteoritic lead samples in which the relative content of Pb\(^{204}\) was considerably higher than the Rosetta Mine sample. In particular, the troilite phase of the Cañon Diablo Meteorite had the composition given in Table 6.32.

A chemical analysis of the lead and uranium content of the troilite phase gave 18 ppm Pb and 0.009 ppm U. The significance of this is that radiogenic lead could not have formed in appreciable quantity after the separation of the troilite phase so that this meteoritic lead may be representative of the composition of primeval lead in the solar system. This conclusion depends on the assumption that meteoritic matter is a true sample of solar material and that the solidification of meteoritic material into separate phases

\(^{236}\) C. Patterson, H. Brown, G. Tilton, and M. Inghram, Phys. Rev. 92, 1234 (1953).
Table 6.32 Relative Atomic Abundances of Lead Fraction of Important Terrestrial and Meteoritic Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pb (^{204})</th>
<th>Pb (^{206})</th>
<th>Pb (^{207})</th>
<th>Pb (^{208})</th>
</tr>
</thead>
</table>
| Rosetta Mine, South Africa  
(Collins, Russell and Farquhar 1953)        | 1             | 12.65         | 14.27         | 32.78         |
| Canon Diablo Meteorite  
Troilite Phase  
(Patterson, Brown, Tilton and Inghram 1953) | 1             | 9.41          | 10.27         | 29.16         |
occurred after element formation in a time short compared to the total time which has elapsed since. Many experimental facts have been cited to substantiate these assumptions.

Radiogenic lead. Any lead formed as the stable end product of the decay of uranium or thorium is referred to as radiogenic lead.

Common (or ordinary) lead. This is lead obtained from non-radioactive lead minerals or from rock-making minerals which accommodate lead in their structures. The constituents of common lead are original lead and varying small amounts of radiogenic lead. In the beginning, all lead was primeval lead. But later radiogenic lead formed from the decay of uranium and thorium and at various times and by various geologic processes, not understood in any clear detail, the lead fractions from various portions of the crust were mixed and redeposited in minerals to give common leads of varying isotopic content.

Primary lead. This is the lead present in a particular mineral at the time of its formation. If the mineral contains appreciable amounts of uranium or thorium, the isotopic composition of this lead will change with time, due to the steady addition of radiogenic lead.

The Chemical Lead-Uranium Method of Mineral Dating. The ultimate products of the decay of natural uranium and thorium are helium and lead as given by the equations

\[
\begin{align*}
U^{238} & \rightarrow 8 \text{He}^4 + \text{Pb}^{206} \\
U^{235} & \rightarrow 7 \text{He}^4 + \text{Pb}^{207} \\
\text{Th}^{232} & \rightarrow 6 \text{He}^4 + \text{Pb}^{208}
\end{align*}
\]

Because of the finite half-lives of the intermediate products, it takes some years before the uranium-lead equilibrium is established; namely \(\sim 10^6\) years, \(\sim 10^5\) years and \(\sim 10^2\) years, respectively, for the three series.

After this length of time, the time variation in the relative amounts of parent and daughter atoms may be expressed as

\[
(\text{Lead daughter})_{\text{Now}} = (\text{Parent})_{\text{Now}} (e^{\lambda t - 1})
\]

where \(\lambda\) is the decay constant of the parent in years\(^{-1}\).

This relationship was first proposed as a means of calculating the ages
of minerals bearing uranium or thorium by the American radiochemist, Bertram Boltwood, working in Lord Rutherford's laboratory. The first minerals were dated by this method in the first decade of this century.\(^{237}\)

In an isolated chemical system such as a mineral, a determination of the amounts of parent and daughter and a knowledge of the rate of decay \(\lambda\) of the parent leads to a solution for the age, \(t\), of the system. In a uranium mineral to which nothing has been added and nothing removed and in which no lead was present when the system originally formed, an age can be found by analyzing for lead and uranium (or thorium) and solving for \(t\). The technique is usually referred to as the chemical lead-uranium (or lead-thorium) method. The word, chemical, in this title means that the amount of lead in the mineral is determined by a chemical analytical technique, but that an isotopic analysis is not performed. Many hundreds of mineral specimens have been dated by this method but a large fraction of these dates are questionable because it has been found that the premises on which the method rests are not valid for most minerals. We consider briefly some of the difficulties and possible sources of error.

1. Most minerals contain a mixture of uranium and thorium so that both elements have to be analyzed quantitatively, since the two elements produce lead at different rates. (The fact that \(U^{235}\) is always present in natural uranium does not cause trouble since the isotopic percentage is so low and does not vary from sample to sample). 2. Lead must be isolated quantitatively and lead contamination from laboratory air, reagents, etc. must be rigorously excluded. 3. The method assumes that the mineral contained no lead at the time of its formation (primary lead); frequently, however, uranium and thorium minerals do contain primary lead so that the apparent age of the mineral is too high. In the evolution of the lead-uranium method, an attempt was made to correct for primary lead by determination of the atomic weight of the lead fraction; since the atomic weight of Ra\(\alpha\) is 206.04 while that of common lead is 207.2, it is possible by very accurate measurement of the atomic weight to estimate the relative amounts of radiogenic and primary lead in the sample. Even with this method, however, the correction is only approximate since the composition of the primary lead is a variable quantity depending on unknown

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factors. A further disadvantage is that the method is limited to minerals from which enough lead can be isolated for the atomic weight determinations. The atomic weight determination has been repolaced by the more accurate mass spectrometric method to be described below.

(4) The method assumes no alteration of the mineral during the geologic period since its formation. Selective leaching of uranium thorium and lead has been noted in many samples. Later addition of lead from other sources can also give erroneous results. It is quite important that the form of the mineral and geologic setting of the specimen be known and considered.

(5) It is necessary to consider the possible loss by diffusion of the emanation isotope in the radioactive chain. This is not a serious problem in the $^\text{235}$U decay chain or in the thorium series since the half-life of the gaseous actinon and thoron are only 3.9 seconds and 52 seconds, respectively. But $\text{Rn}^{222}$ has a half-life of 3.8 days; hence, if the structure of the uranium-bearing mineral is such that an appreciable amount of the gaseous product could have diffused away during a period of a few days, there might have been an appreciable reduction in the amount of $\text{Pb}^{206}$ produced in the mineral.

Because of these difficulties, the chemical lead-uranium method has had limited success and is in disrepute. The essential simplicity of the method is appealing and some modern workers have found it to be reliable when applied to a few fairly common minerals (zircon, zenotime and some monazites) which are resistant to chemical change and which were nearly completely free of lead content at the time of their formation.

The Mass Spectrometric Lead-Isotope and Lead-lead Methods of Mineral Dating. Determination of the isotopic composition of the lead daughter fraction is now considered essential. This determination can be made by atomic weight measurements or by hyperfine structure methods, but more usually is made with the mass spectrometer. The isotopic analysis plus a quantitative analysis for lead, thorium and uranium makes it possible in principle to calculate the age of the mineral in the four different ways summarized in the following equations:

$$ N_{\text{Pb}-206} = N_{\text{U}-238} (e^{\lambda_{238}t} - 1) \quad (3a) $$

$$ N_{\text{Pb}-207} = N_{\text{U}-235} (e^{\lambda_{235}t} - 1) \quad (3b) $$
The symbol N refers to the number of atoms of the indicated nuclides present at the time of analysis. The number of atoms of the lead isotopes must be corrected for primeval lead before the calculation is made. The required decay constants \( \lambda \) are tabulated in Table 6.33.

The first three equations represent the three lead-isotope methods, whereas the fourth constitutes the basis of the lead-lead method. The lead-lead calculation is not independent of the other three. The lead-lead method is based on the fact that \( U^{238} \) and \( U^{235} \) decay at rates differing by a factor of 6.3 so that the ratio of their stable end-products \( \frac{Pb^{207}}{Pb^{206}} \) varies systematically with the age of the radioactive mineral. See Fig. 6.47. In the application of equation (3d), it is not necessary to determine the ratio \( \frac{U^{238}}{U^{235}} \) since this is simply the abundance ratio of natural uranium which is constant for all uranium samples (139 as determined by Nier in 1939, or 138 as determined by Lounsbury in 1956). Nor is it necessary to determine the quantity of lead accurately since only the ratio of the lead isotopes appears in the equation. Hence, the lead-lead method is one of extreme simplicity.

However, the lead-lead method can give erroneous results if the correction for primary lead is incorrectly made or if alteration effects have occurred in the mineral being dated. For example, appreciable loss of radon from the mineral would cause incomplete deposition of \( Pb^{206} \) and hence a high apparent age. Therefore, it is desirable to crosscheck the age by an independent determination made by one or more of the other equations (3a) through (3c) or by the Rb\(^{87}\) - Sr\(^{87}\) or K\(^{40}\) - Ar\(^{40}\) methods discussed below. If the results agree one can be more confident of the result; if they do not agree, the pattern of disagreement may help to locate the cause of the disagreement. The use of the lead isotope methods requires quantitative analysis for lead and uranium and thorium. The chemical recovery factor for lead fractions can be determined mass spectrometrically by the isotope dilution method. For
Table 6.33 Decay Constants Required in Age Calculations

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-Life</th>
<th>Disintegration constant, λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>U$^{238}$</td>
<td>$4.51 \times 10^9$ years</td>
<td>$1.537 \times 10^{-10}$ years$^{-1}$</td>
</tr>
<tr>
<td>U$^{235}$</td>
<td>$7.13 \times 10^8$ years</td>
<td>$9.72 \times 10^{-10}$ years$^{-1}$</td>
</tr>
<tr>
<td>Th$^{232}$</td>
<td>$1.39 \times 10^{10}$ years</td>
<td>$4.99 \times 10^{-11}$ years$^{-1}$</td>
</tr>
</tbody>
</table>
some reasons, not clearly understood, the $^{208}\text{Pb-}^{232}\text{Th}$ method seldom gives results in agreement with the other methods and hence cannot be relied on. There is some evidence that $^{208}\text{Pb}$ is more readily leached from the mineral crystal sites previously occupied by the thorium parent, thus leading to too low ages. It should also be noted that the determination of $^{208}\text{Pb}$ often involves a correction for primary $^{208}\text{Pb}$ which often amounts to ten percent of the total.

The mass spectrographic analysis of the lead fraction puts the correction for primary lead on a more secure basis because the abundance of non-radiogenic $^{204}\text{Pb}$ can be used as a guide to the primary lead content. When the $^{204}\text{Pb}$ content is negligible, no correction need be made to the lead isotope ratio and the calculated age is subject to error only from alteration effects. When the $^{204}\text{Pb}$ content is appreciable, its abundance is used together with an estimate of the common lead composition for lead in igneous rocks of that particular age in that particular part of the earth's crust.

Figure 6.47 shows the variation in the isotope ratios as a function of age for the three most used methods. The lead isotope and lead-lead methods received their first real impetus from the splendid mass spectrographic exploratory work of NIER at the end of the 1930's. The method underwent rapid development in the early 1950's when advances in chemical techniques and extension of mass spectrometer sensitivity by orders of magnitude made it possible to apply the method to a very wide range of igneous rocks. By 1960 it had become clear that one class of uranium minerals, namely the uraninites, most often gives concordant ages when determined by two or more methods. Hence, for uraninites the lead-isotope methods are of certified reliability. For a wide variety of other uranium-bearing minerals the wide distribution of age measurements achieved by two or more methods has been discouraging. However, even in these cases the direction of the discordance may give interesting hints on the geological alteration of minerals since their time of formation.

For a fuller account of these methods and their application to geophysical problems consult the references given in the bibliography at the end of this section.

The $^{210}\text{Pb}$ Method of Mineral Dating. The age of an uranium-bearing mineral can be determined by the ratio of any one of the members of the decay
Fig. 6.47. Curves showing the atomic ratios \(\text{Pb}^{207}/\text{U}^{235}\), \(\text{Pb}^{206}/\text{U}^{238}\), \(\text{Pb}^{206}/\text{Th}^{232}\) and \(\text{Pb}^{206}/\text{Pb}^{207}\) in minerals which have been undisturbed for the number of years given by the abscissa and which contained no primary lead. It is important to note that both the numerator and the denominator in all ratios refer to the species present at the time of the analysis.
series to the stable lead end-product provided the series is in equilibrium. The Pb\textsuperscript{206}/U\textsuperscript{238} and Pb\textsuperscript{207}/U\textsuperscript{235} methods just discussed may be taken as examples. Equally good, theoretically, would be such ratios as Pb\textsuperscript{206}/Ra\textsuperscript{226}, Pb\textsuperscript{206}/Io\textsuperscript{230}, Pb\textsuperscript{206}/Po\textsuperscript{214} or Pb\textsuperscript{206}/Po\textsuperscript{210}. However, the evaluation of each ratio involves practical difficulties; the half-lives may be inconveniently short or the chemical purification may be troublesome. The Pb\textsuperscript{206}/Po\textsuperscript{210} (RaD) method, first suggested by HOUTERMANS	extsuperscript{238} and first tested by BEGEMANN and CO-WORKERS	extsuperscript{239} is uniquely satisfactory for several reasons.

1. It is not necessary to carry out a quantitative analysis for uranium or lead.
2. The radioactivity measurement is straightforward.
3. It is unlikely that the lead fraction will be contaminated with other radioactive members of the series since any uranium series member which is not quantitatively removed has either such a short half-life that it will decay before the sample is counted or such a long half-life that the activity will be negligible.
4. The half-life of Po\textsuperscript{210} is 22 years.
5. The Pb\textsuperscript{206}/Po\textsuperscript{210} age is not badly affected by uranium leaching late in the history of the mineral because Po\textsuperscript{210} should be in equilibrium with the 80,000 year ionium long after an appreciable amount of uranium has been leached out.
6. The chemical steps are not complicated and chemical handling is minimal since the spectrometer analysis and the radiation counting can be done on the same sample.
7. The Po\textsuperscript{210} age is independent of radon leakage if radon loss has been constant, since the yield of Po\textsuperscript{210} and Pb\textsuperscript{206} are reduced proportionately.

The amount of Po\textsuperscript{210} is a monitor of the amount of uranium in the mineral via the equilibrium expression,

---

\[(N\lambda)_{\text{Pb-210}} = (N\lambda)_{\text{U-238}}\]

where \(N\) refers to the number of atoms and \(\lambda\) to the decay constant.

The counting of the disintegrations of \(\text{Pb-210}\) requires consideration of the sequence:

\[
\begin{align*}
\text{Pb}^{210} & \quad \text{22 years} \quad \rightarrow \quad \text{Bi}^{210} \\
(\text{RaD}) \quad \text{weak } \beta^- & \quad \rightarrow \quad \text{Po}^{210} \\
(\text{RaE}) & \quad \text{5 days} \quad \rightarrow \quad \text{Po}^{210} \\
(\text{RaF}) & \quad \alpha \quad \rightarrow \quad \text{Pb}^{206} \\
(\text{RaG}) 
\end{align*}
\]

The weak beta particles of RaD cannot be counted, but if the sample is set aside for a few weeks until RaE is in equilibrium, the strong beta particles of RaE are easily counted. Alternatively, the alpha particles of polonium can be observed to grow in and the growth can be compared with standard growth curves. The properties of a RaDEF mixture are discussed in Sec. 6.2 of this chapter.

If no common lead and no appreciable amount of thorium is present in the mineral, the fraction of \(\text{Pb}^{206}\) may be estimated to a few percent without mass analysis for comparatively young samples. In most cases, however, these uncertainties are much too large so that mass spectrometric measurement of the isotopic composition is imperative to obtain reliable results.

The Pb-210 method is a useful alternative or supplement to the lead-uranium or lead-lead methods. KOMAN and Saito, T. Kohman and N. Saito, Ann. Rev. of Nuc. Sci. 4, 418 (1954).
Holmes Computation of the Age of the Earth. In 1946 HOLMES\textsuperscript{241} proposed an ingenious method for the estimation of the age of the earth's crust based on the analysis of many lead minerals carried out by NIER.\textsuperscript{242} This method is based on the following model for the formation of lead minerals.

(1) Primeval lead had a uniform composition throughout the earth up to the time the crust was formed.

(2) When the crust was formed the Pb/U and Pb/Th ratios in different areas varied slightly, were frozen at a particular value for any one region, and did not subsequently vary through any geologic process from that time until the present, except for radioactive decay.

(3) Each lead ore has been derived from one such area and has not been mixed with lead from any other source. At the time of the formation of the lead mineral no uranium or thorium was deposited with the lead so that no radiogenic lead has been added since the formation of the mineral. Hence, the isotopic analysis should serve as a record of the isotopic composition of the common lead in the magma of that region at the time of formation of the lead mineral.

(4) The age of the lead mineral can be determined by stratigraphic correlations or by dating nearby uranium-bearing minerals.

We let $x_m$ and $y_m$ be the abundance of Pb\textsuperscript{206} and Pb\textsuperscript{207}, respectively, relative to Pb\textsuperscript{204} in the mineral sample today and $x_o$ and $y_o$ be the same quantities at the time, $t_o$, when the earth's crust was formed. We define $V_m$ as the ratio of atoms of U\textsuperscript{235} relative to Pb\textsuperscript{204} in the sample today. This is not an universal constant for the entire crust but applies to the isolated geologic region within which a particular lead mineral was formed. The quantity $\alpha$ is defined as the ratio of U\textsuperscript{238} to U\textsuperscript{235} at the present time; $\alpha$ is 139. The time elapsed since formation of the earth's crust is represented as $t_o$ and the time of deposition (dating backward from the present) of the lead ore is taken as $t_m$. With these definitions and the above assumptions the laws of radioactive

\textsuperscript{241} A. Holmes, Nature 157, 680 (1946); 159, 127 (1947); 163, 453 (1949).
\textsuperscript{242} A. Nier, J. Am. Chem. Soc. 60, 1571 (1938); Nier, Thompson and Murphey, Phys. Rev. 60, 112 (1941).
decay lead directly to the following equations:

\[ x_m = x_o + \alpha v_m (e^{\lambda_{238}t_o} - e^{\lambda_{238}t_m}) \]  \hspace{1cm} (5a)

\[ y_m = y_o + \alpha v_m (e^{\lambda_{235}t_o} - e^{\lambda_{235}t_m}) \]  \hspace{1cm} (5b)

Equations 5a and 5b give in an \( \alpha, x_m, y_m \) diagram the "lines of the lead development" for constant values of \( v_m \) as a function of time. Dividing the two equations we get:

\[ \frac{x_m - x_o}{y_m - y_o} = \frac{\alpha(e^{\lambda_{238}t_o} - e^{\lambda_{238}t_m})}{(e^{\lambda_{235}t_o} - e^{\lambda_{235}t_m})} \]  \hspace{1cm} (5c)

This equation yields a family of straight lines (isochrones) corresponding to different values of \( t_o \). These lines intersect at the point \( x_o, y_o \) corresponding to the isotopic composition of primeval lead.

Several authors have used NIER's \( ^{242}\text{Pu} \) data on the isotopic composition and age of formation of lead minerals to calculate an age of the earth and the composition of primeval lead. The calculation is made graphically or by least squares fit to equation (5). Some results are summarized in Table 6.34.

For many years the value \((3.3 \pm 0.3) \times 10^9\) years, obtained by this method was generally accepted as the age of the earth's crust. It was also considered an approximate measure of the time since the formation of the elements, since there was some reason to believe that the time elapsed from nucleogenesis to the formation of the earth was short compared to 3.3 billion years. However, the figure arrived at by this method has never been accepted without reservations since the assumptions upon which it is based are unproved and the extrapolations involved are extreme. Particularly disturbing is the fact that not all the mass spectrographic data on the lead minerals is included in the calculations, about one third of the data being rejected as anomalous. The values listed in Table 6.34 could be regarded as meaningful as long as no lead mineral had values of \( x_m \) and \( y_m \) less than the \( x_o \) and \( y_o \) values in this table. When the meteoritic lead abundances listed in Table
Table 6.34 Estimates of Age of Earth's Crust (Lithosphere) by HOLMES' method

<table>
<thead>
<tr>
<th>Author</th>
<th>( t_o )</th>
<th>( \frac{x_o}{x_{o_0}} )</th>
<th>( \frac{y_o}{y_{o_0}} )</th>
<th>( \frac{z_o}{z_{o_0}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOLMES 1947</td>
<td>( 3.35 \times 10^9 ) years</td>
<td>10.95</td>
<td>13.51</td>
<td>---</td>
</tr>
<tr>
<td>HOUlTERMANS 1947</td>
<td>( 2.9 \times 10^9 ) years</td>
<td>11.52</td>
<td>14.03</td>
<td>31.6</td>
</tr>
<tr>
<td>BULLAR and STANLEY 1949</td>
<td>( 3.29 \times 10^9 ) years</td>
<td>11.86</td>
<td>13.86</td>
<td>---</td>
</tr>
<tr>
<td>COLLINS, RUSSELL FARQUHAR* 1953</td>
<td>( 3.5 \times 10^9 ) years</td>
<td>11.33</td>
<td>13.55</td>
<td>31.10</td>
</tr>
</tbody>
</table>

* In addition to NIER'S 1940 data COLLINS, RUSSELL and FARQUHAR considered new data of their own on lead minerals.
were reported by PATTERSON, BROWN, TILTON and INGHRAM in 1953 it became almost certain that the age calculated by the HOLMES method was too low.

Because of the uncertainties in the HOLMES assumptions, certain authors have preferred to use a somewhat similar calculation based on the NIER data to calculate only a maximum age of the elements. In this approach one calculates backwards in time to determine at what time the amount of one of the three isotopes Pb\(^{206}\), Pb\(^{207}\) or Pb\(^{208}\) drops to zero since obviously a negative quantity (negative value of \(x_0\) or \(y_0\)) is physically inadmissible. ALPHER and HERMAN using NIER\'S data, calculate that the Pb\(^{206}\) ratio drops to zero at a time \(~5.3 \times 10^9\) years. COLLINS, RUSSELL and FARQUHAR using more extensive data calculate that the first ratio to drop to zero is Pb\(^{207}/\)Pb\(^{204}\), and calculate a maximum age of \(~5.5 \times 10^9\) years.

**Calculation of the Age of the Earth. (From Lead Data on Meteoritic and Terrestrial Lead Samples).** BROWN proposed that lead isolated from meteorites might be used as a measure of the isotopic composition of lead at the time of formation of the solar system. The data of PATTERSON ET AL on meteoritic leads probably reveals the true composition of primeval lead. See Table 6.32. We can use these data to calculate the age of the earth as follows.

Let us define \(x_0\) and \(y_0\) as the ratios Pb\(^{206}/\)Pb\(^{204}\) and Pb\(^{207}/\)Pb\(^{204}\), respectively, in primeval lead and set them equal to the lead ratios found in the troilite phase of the Cañon Diablo Meteorite. (Table 6.32) Let us further define \(x_m\) and \(y_m\) as the corresponding ratios for recent common leads isolated from the surface of the earth. The constant \(\alpha\) is taken equal to 139 and is the ratio of U\(^{238}\) atoms to U\(^{235}\) atoms in present day uranium. We can then write.

\[
\frac{x_m - x_0}{y_m - y_0} = \frac{\alpha (e^{\lambda t_{o-1}})}{e^{\lambda t_{o-1}}} \tag{6}
\]

---

we can solve this equation for $t_0$, the age of the earth, if we have a reliable
value for $x_m$ and $y_m$. Equation (6) is very similar to equation (5c) if one
notes that $t_m$ in the present case is zero so that $e^{\lambda t_m} = 1$.

Nearly all analyzed terrestrial lead samples (except those from uranium
minerals) that have been isolated from their uranium environments since tertiary
times ($<30$ million years ago) have $x_m$ and $y_m$ values which fall within the
ranges:

\[ x_m = 18.07 - 18.95 \]
\[ y_m = 15.40 - 15.76 \]

Substitution of these values into equation (6) leads to a value of approximately
$4.5 \times 10^9$ years for $t_0$. A very useful type of lead sample is that found in
deep sea sediments particularly in the sediments known as manganese nodules.
These nodules grow at a very slow rate and the lead deposited in them must
constitute a reliable sampling of the lead eroded from enormous masses of con­
tinental rock and washed ultimately into the sea from enormous volumes of sur­
face drainage waters. Table 6.35 lists the composition of present day common
lead as determined from such deep sea samples. These values of $x_m$ and $y_m$
again lead to an age of the earth of $4.5 \times 10^9$ years. This calculation assumes
that earth matter came from the same source as did that of the meteorites.

Another calculation based on equation (6) can be made from the lead
isotope data obtained from a variety of meteorites. If we make the assump­
tion that all meteorites were condensed at about the same time from matter
which had a uniform isotopic composition of lead then all present-day lead­
isotope ratios should fit equation (6) with a constant value for $t_0$. The lead
isotope ratios in different meteorites may be greatly different because of
their differing content of uranium, but the ratios should differ in a systema­
tic way. Figure 6.48 illustrates this. This figure shows that a $^{206}$Pb-$^{207}$Pb
"isochron" with a $t_0$ value of $4.61 \times 10^9$ years fits a wide variety of data
from meteorites as well as terrestrial oceanic lead.

Table 6.35 Composition of Present Day Common Lead as Determined in Lead Isolated from Deep Sea Sediments (Manganese Nodules)*

\[
\begin{align*}
{x}_m &= \frac{\text{Pb}^{206}}{\text{Pb}^{204}} = 18.91 \\
{y}_m &= \frac{\text{Pb}^{207}}{\text{Pb}^{204}} = 15.69 \\
{z}_m &= \frac{\text{Pb}^{208}}{\text{Pb}^{204}} = 38.68
\end{align*}
\]

Fig. 6.48. A plot of the lead isotope ratios observed in terrestrial oceanic lead and in a variety of meteorites, showing agreement with a $\text{Pb}^{206} - \text{Pb}^{207}$ isochrone with a $t_0$ value of $4.6 \times 10^9$ years. Figure prepared by J.H. Reynolds from data of Patterson et al., Marshall and Hess, and others. In the terminology of equation (6), the abscissa and ordinate are $x_m$ and $y_m$, respectively. The agreement of the data with the straight line suggests that all meteorites and the earth belong to a common "array" of bodies which were separated out from matter containing a common primordial lead composition about $4.6 \times 10^9$ years ago.
An excellent check on this age figure for meteorites has been obtained by dating meteorites by the $^{40}$K - $^{40}$Ar and the $^{87}$Rb - $^{87}$Sr methods described below. Results in the range 4.3 to 4.8 billions years have been obtained on several meteorites.

At the present time it is a widely held view that meteorites and the earth's crust (lithosphere) condensed out of the same "batch" of elementary material and that both formed condensed phases at about the same time, namely about 4.5 billion years ago. This age is not identical with the age of the elements since nucleogenesis may have been completed at a significantly earlier time than that of the formation of the lithosphere. Furthermore, nucleogenesis itself may have required a quite significant period of time. The latter is a strong function of the cosmological model of nucleogenesis which is adopted and we shall not discuss these models here other than to call attention to the fact that some modern models suggest a period of the order of $10^{10}$ years for the duration of the element-forming process. The time elapsed since the end of the element forming process and the condensation of matter in our solar system can be estimated experimentally by an interesting method which we can discuss briefly. This method depends upon the discovery by Reynolds\textsuperscript{249-251} of a great excess of Xe\textsuperscript{129} in the Xenon fraction isolated from the chondritic (stone) meteorite, Richardton, and later from the enstatite chondrite, Indarch.\textsuperscript{251} This excess Xe\textsuperscript{129} is believed to be the decay product of I\textsuperscript{129} originally present in the meteorite but now completely extinct because of its relatively short $1.7 \times 10^7$ year half-life. The presence of the excess Xe\textsuperscript{129} in itself indicates that the condensation of the meteoritic mass to a condition which could retain xenon must have occurred in a time roughly of the order of magnitude of $10^7$ years after the last element forming process had occurred. In order to measure this period more definitely the following quantitative information is required.

(1) The ratio of stable $\text{Xe}^{129}$ to stable $\text{I}^{127}$ in the meteorite plus the assurance or assumption that no $\text{Xe}^{129}$ has been lost during the 4.5 billion year lifetime of the meteorite. This ratio was measured by Reynolds by quantitative neutron activation analysis and mass spectrometry.

(2) The ratio of radioactive $\text{I}^{129}$ to stable $\text{I}^{127}$ at the end of nucleogenesis. This ratio cannot be obtained directly and must be estimated by an examination of systematic trends in the isotopic abundance figures and a consideration of possible nuclear models. If nucleogenesis took a short time compared to the $\text{I}^{129}$ half-life, the ratio $(\text{I}^{129}/\text{I}^{127})_0$ was probably about 1. If nucleogenesis took a long time compared to $10^7$ years the primordial $\text{I}^{129}$ stock would have leveled off while the $\text{I}^{127}$ content would have continued to rise.

In this case $(\text{I}^{129}/\text{I}^{127})_0$ might have attained the value equal to the mean life of $\text{I}^{129}$ divided by the duration of nucleosynthesis. Following a suggestion of CAMERON, REYNOLDS chose the effective value of $2 \times 10^{10}$ years and arrived at a value for $(\text{I}^{129}/\text{I}^{127})_0 = 0.00125$.

The time period whose calculation we are now discussing is given by the expression

$$\Delta t = \frac{T_{1/2}(\text{I}^{129})}{0.693} \left[ \ln \left( \frac{\text{I}^{127}/\text{Xe}^{129}}{\text{I}^{127}/\text{I}^{127}} \right)_{\text{meteorite}} + \ln \left( \frac{\text{I}^{129}/\text{I}^{127}}{\text{I}^{129}/\text{I}^{127}} \right)_0 \right] \quad (8)$$

We note that an error of a factor of 10 in either ratio leads to only a 16 percent error in $\Delta t$.

Reynolds has calculated preliminary values of 120 million years for $\Delta t$ from the data taken on the Richardton meteorite and 86 million years for data from the meteorite, Indarch. The exact meaning of this time interval measured by the $\text{Xe}^{129}$ excess is given different interpretations by the different experts who have discussed it. It is beyond the scope of our interest to pursue the matter further here or to enter into the large question of the course and duration of the element formation process. Ideas about cosmology and nucleosynthesis are undergoing many changes at the present time.

252. A.G.W. Cameron, private communication to J.R. Reynolds.
Dating Methods Based on the Radioactivity of Rubidium and Potassium.

In this chapter we are concerned chiefly with the heavy element series of natural radioactivities and their use in dating of minerals. No summary of dating methods for older minerals would be complete, however, without a mention of the K\(^{40}\) - A\(^{40}\) and Rb\(^{87}\) - Sr\(^{87}\) methods. We shall not review C\(^{14}\) dating which applies to quite recent dates, comparatively speaking, i.e., up to 30,000 years.

The isotope, Rb\(^{87}\) decays by beta emission to stable Sr\(^{87}\) with a half-life of 5.0 \(\times 10^{10}\) years (decay constant = 1.39 \(\times 10^{-11}\) yr\(^{-1}\)). The isotopic content of Rb\(^{87}\) in natural rubidium is 27.8 percent. The principle of mineral dating by the Rb\(^{87}\) - Sr\(^{87}\) method is very simple; one merely determines the total amount of rubidium and the total amount of Sr\(^{87}\) in the mineral, and applies the law of radioactive decay. For the success of the method it is necessary to establish that no selective elution of rubidium or strontium occurred since the formation of the mineral. It is also necessary that the amount of non-radiogenic strontium in the mineral be low and it is essential that the half-life of Rb\(^{87}\) be known accurately. The soft beta particle emitted by Rb\(^{87}\) seriously delayed the determination of an accurate decay constant and reduced the reliability of the method until recent years. A detailed review of this point is given by ALDRICH and WETHERILL.\(^{253}\)

HAHN, STRASSMAN and WALLING\(^{254}\) first found radiogenic strontium in lepidolite, the mineral with the highest rubidium concentration and HAHN and WALLING\(^{255}\) made the first age determinations by this method in 1938. The method was placed on a much firmer basis in 1953 by the introduction of the isotopic dilution mass spectrometric procedure.\(^{256-257}\) All modern Rb - Sr


\(^{254}\) O. Hahn, F. Strassmann and E. Walling, Naturwiss 25, 189 (1937).

\(^{255}\) O. Hahn and E. Walling, Chem. Z. 67, 55 (1938).


age determinations include isotopic analysis of the strontium and correction for non-radiogenic Sr\(^{87}\).

The second method we are discussing is based on the decay scheme of K\(^{40}\) which is shown in Fig. 6.49. Potassium 40 is a rare isotope of potassium which occurs in natural potassium only to the extent of 0.0119 percent. It decays 11 percent by electron capture to form Ar\(^{40}\). One of the attractions of the K\(^{40}\) - Ar\(^{40}\) methods is that argon can be easily studied in a mass spectrometer.

Because of the branching decay the mathematical expression which is used to compute the age of the mineral is somewhat more complicated than in the Rb\(^{87}\) - Sr\(^{87}\) case. This expression may be written as follows:

\[
t = \frac{1}{\lambda_{\text{ec}} + \lambda_{\beta}} \ln \left( 1 + \frac{\lambda_{\text{ec}} + \lambda_{\beta}}{\lambda_{\text{ec}}} \frac{A_{\text{Ar}}^{40}}{A_{\text{K}}^{40}} \right).
\]

where \(\lambda_{\text{ec}}\) and \(\lambda_{\beta}\) are the respective decay constants for electron capture and beta decay, and \(A_{\text{K}}^{40}/A_{\text{Ar}}^{40}\) is the atom ratio of the nuclides in the mineral.

The K\(^{40}\) - Ar\(^{40}\) method developed slowly because of certain experimental difficulties and because of the great difficulties involved in an exact determination of the decay constants. These have been largely overcome and the method has recently taken its place as one of the most reliable and generally useful of the dating methods. A good review of the measurements of the K\(^{40}\) radiations is given by ALDRICH and WETHERILL.\(^{253}\) The principal remaining uncertainty is whether there is a slight unobserved electron capture decay directly to the ground state of Ar\(^{40}\).

The dating method consists in determining quantitatively the potassium content and argon content of a potassium-bearing mineral. The argon content must be corrected for non-radiogenic argon. It is assumed that argon diffusion is insignificant, an assumption which has been checked by dating potassium minerals associated with other minerals which were independently dated by the lead methods. Results show that argon retention is quantitative in micas but often incomplete in feldspars. It is not surprising that argon diffusion loss is low since recoil effects are insignificant and, although argon is a large atom, it presumably occupies a site previously occupied by the large K\(^{+}\) (1.33 \(\text{Å}\)) and hence, does not cause undue strain in the structure,
Fig. 6.49. Decay scheme of potassium 40.
particularly as the ratio of argon to potassium atoms is never large.

The first argon age determinations were reported by SMITS and GENTNER\textsuperscript{258} in 1950. The method was improved by introduction of the isotopic-dilution mass spectrometric technique by WASSERBURG and HAYDEN\textsuperscript{259}. The argon method appears capable of wide application for dating igneous rock. It can be applied to micas and feldspars which are ubiquitous minerals. It has been applied also to the dating of meteorites, as was mentioned above. Results indicate an age of 4.3 to 4.8 billion years in excellent agreement with the lead-lead ages of meteorites.\textsuperscript{248}

The Helium Age Methods. Helium was first identified in the sun's spectrum and was first discovered in terrestrial materials in 1895 when RAMSAY identified helium gas in uranium and thorium-bearing minerals. The constant association of helium with radioactive minerals helped later to confirm the identification of alpha particles with ionized rapidly-moving helium. RUTHERFORD suggested that the amount of helium in radioactive minerals might be a means of measuring geologic time and LORD RAYLEIGH soon afterwards began research on the content of helium in pitchblende and thorianite.

Since those early years there has been a continuing interest in the helium content of minerals and a formidable number of samples have been analyzed in many laboratories. Unfortunately, the helium age method frequently gives low results when checked against other dating methods, mainly because of loss of helium. The causes of this helium loss are complex and a major part of the helium analysis work has been devoted to study of helium migration and loss in various types of minerals.

We shall not discuss the helium age measurements further in this book. The interested reader is referred to an extensive review by HURLEY.\textsuperscript{260}

Bibliography on Nuclear Geology. The entire subject of nuclear geology is a fascinating subject now under very rapid development. The heavy elements play an important role in this research field. The dating of minerals by lead isotope methods and the study of ionium and radium content in ocean sediments are some examples of the applications. It is beyond the scope of this book to discuss all applications of heavy element studies to geology. The appended bibliography may serve as a guide to further reading.
GENERAL BIBLIOGRAPHY ON NUCLEAR GEOLOGY


6.6 THE NATURAL OCCURRENCE OF TRANSURANIUM ELEMENTS IN TRACE AMOUNT

Pu\(^{239}\) in Nature. Pu\(^{239}\) has a half-life of 24,000 years so that any primordial plutonium would long since have decayed to form U\(^{235}\). However, in uranium-bearing minerals the action of natural neutrons may cause the formation of small quantities of plutonium via the sequence

\[ \text{U}^{238} + n \rightarrow \text{U}^{239}, \quad \text{U}^{239} \beta^- \rightarrow \text{Np}^{239} \beta^- \rightarrow \text{Pu}^{239}. \]

This was first proven experimentally in 1942 by G.T. SEABORG and M.L. PERLMAN\(^{261}\) who chemically separated the plutonium from a sample of Canadian pitchblende concentrate and conservatively estimated the plutonium content of the ore to be roughly one part in \(10^{14}\) by weight. From considerations of possible methods of formation of plutonium it was assumed that the plutonium was Pu\(^{239}\). Similarly, GARNER, BONNER and SEABORG\(^{262}\) searched in 1942 for naturally occurring plutonium in carnottite, hatchettolite and fergusonite. They found Pu\(^{239}\) present in carnottite to the extent of about one part in \(10^{14}\) and were able to set an upper limit for the amount of plutonium in fergusonite of one part in \(10^9\).

Later when the chemical properties of plutonium and the instrumental techniques for alpha activity detection and analysis were better understood, LEVINE and SEABORG\(^{263}\) studied this problem more thoroughly. Plutonium was separated in known yield from the uranium minerals listed in Table 6.36 and identified by alpha spectrum analysis as Pu\(^{239}\).

PEPPARD and his CO-WORKERS\(^{264}\) isolated microgram quantities of plutonium from the aqueous wastes left in the processing of ton quantities of

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Table 6.36 Plutonium Occurring in Radioactive Minerals
Levine and Seaborg

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Uranium content %</th>
<th>Ratio Pu$^{239}$ to ore (by weight)</th>
<th>Ratio Pu$^{239}$ to U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canadian pitchblende</td>
<td>13.5</td>
<td>9.1 x 10^{-13}</td>
<td>7.1 x 10^{-12}</td>
</tr>
<tr>
<td>Belgian Congo pitchblende</td>
<td>38</td>
<td>4.8 x 10^{-12}</td>
<td>12 x 10^{-12}</td>
</tr>
<tr>
<td>Belgian Congo pitchblende†</td>
<td>45.3</td>
<td>7.0 x 10^{-12}</td>
<td>15 x 10^{-12}</td>
</tr>
<tr>
<td>Colorado pitchblende</td>
<td>50</td>
<td>3.8 x 10^{-12}</td>
<td>7.7 x 10^{-12}</td>
</tr>
<tr>
<td>Brazilian monazite</td>
<td>0.24</td>
<td>2.1 x 10^{-14}</td>
<td>83 x 10^{-12}</td>
</tr>
<tr>
<td>N. Carolina monazite</td>
<td>1.64</td>
<td>5.9 x 10^{-14}</td>
<td>3.6 x 10^{-12}</td>
</tr>
<tr>
<td>Colorado fergusonite</td>
<td>0.25</td>
<td>&lt;1 x 10^{-14}</td>
<td>&lt;4 x 10^{-12}</td>
</tr>
<tr>
<td>Colorado carnotite</td>
<td>1.0</td>
<td>&lt;4 x 10^{-14}</td>
<td>&lt;0.4 x 10^{-12}</td>
</tr>
</tbody>
</table>

† Peppard et al., Ref. 264.
Belgian Congo pitchblende. They found one part $^{239}\text{Pu}$ per $1.4 \times 10^{11}$ parts of the pitchblende concentrate (45.3% uranium). This plutonium was analyzed carefully by differential pulse height analysis of the alpha spectrum, by neutron irradiation studies and by mass spectrometry, and no plutonium isotope other than $^{239}\text{Pu}$ was found.

Possible sources of neutrons to account for this natural production of plutonium include:

1. the spontaneous fission of uranium
2. $(\alpha,n)$ reactions caused by the action of alpha particles from the heavy elements on the nuclei of light elements in the ore
3. cosmic rays
4. induced fission of $^{235}\text{U}$.

In the case of pitchblende ores the first two sources are of comparable importance. In thorium ores neutrons from $(\alpha,n)$ reactions are probably dominant. Cosmic rays appear to contribute a negligible number of neutrons by comparison.

LEVINE and SEABORG have estimated the relative importance of these neutron sources very crudely in the following way.

"Assuming an average of two neutrons per fission, and a spontaneous fission decay constant of $1.1 \times 10^{-16}$ per year for $^{238}\text{U}$, we calculate that about 1.1 neutrons per gram of uranium are emitted per minute due to spontaneous fission. A 100-g. sample of ore containing 13.5% uranium will emit about 15 neutrons per minute by this means.

As suggested previously, there is another source of neutrons to be considered. One gram of uranium and the decay products in equilibrium with it emit about $6 \times 10^6$ alpha particles per minute whose maximum energies range from 4.2 to 7.68 MeV. These alpha particles, impinging on the nuclei of the light elements present, cause reactions whereby neutrons are emitted $(\alpha,n$ reactions). ROBERTS has reported on the number of neutrons emitted when thick samples of the light elements are bombarded with 5.3 MeV alpha particles.

STUHLINGER\textsuperscript{267} has given the excitation functions for the neutron emitting reactions involving alpha particles on boron and beryllium with alpha particle energies up to 8.8 MeV. With these data and those of others,\textsuperscript{268,272} the number of neutrons emitted per alpha particle (of a given energy) impinging on a target of a light element can be estimated. Using the chemical analysis of a sample of Canadian pitchblende reported by MARBLE,\textsuperscript{273} it can be calculated that in a 100-g. sample of ore containing 13.5\% uranium, fifteen to twenty neutrons per minute will be formed due to the action of alpha particles on the nuclei of the light elements in the ore (\(\alpha, n\) reactions). However, if, for example, as much as 1\% of beryllium, boron, or lithium is present in the ore in addition to the elements reported in the analysis, the additional neutron yields due to (\(\alpha, n\)) reactions in such a 100-g. sample would be about 100, 40 and 10 neutrons per minute, respectively.

MONTGOMERY and MONTGOMERY\textsuperscript{274} have estimated the neutron intensity at sea level in the cosmic radiation to be about 0.1 neutron per cm\(^2\) per minute. Although the actual cosmic ray neutron intensity in the ores may be somewhat higher than this (due to the action of other types of cosmic rays on the ore), the neutron contribution from cosmic rays to the total neutron flux in the ores seems small.

For a typical 100-g. sample of pitchblende ore containing 13.5\% uranium, then, somewhat more than some thirty neutrons per minute are available from the sources mentioned above. Simple calculations show that the U\textsuperscript{238} in this sample must capture some ten to fifteen neutrons per minute, or something less than about 30 to 50\% of those available, in order to account for an equilibrium concentration of one part Pu\textsuperscript{239} per 1.4 x 10\textsuperscript{11} parts uranium. A

\begin{thebibliography}{999}

\textsuperscript{267} E. Stuhlunger, Z. Physik \textbf{114}, 185 (1939).
\textsuperscript{270} I.H. Halpern, Phys. Rev. \textbf{74}, 1234 (1948).
\textsuperscript{271} L.N. Ridenour and W.J. Henderson, \textit{Ibid.}, 889 (1937).
\end{thebibliography}
consideration of the neutron absorption cross sections of the elements in the ore, together with their abundances from the above mentioned analysis, indicates that absorption of this fraction of the neutrons by the uranium is reasonable.

It should be emphasized that these estimations of the neutron flux are necessarily quite approximate. Thus, values for the spontaneous fission decay constant of $^{238}\text{U}$, varying from about half to twice the value quoted and used above, have been reported.\(^{275-277}\) Similarly, the estimation of the neutron flux from the $(\alpha,n)$ reactions is subject to error due to the uncertainty of the composition of the ores and the lack of precise knowledge for the yields of the $(\alpha,n)$ reactions; the estimation of the numbers of neutrons from this source could be in error by a factor of two or possibly even more. Therefore, the relative importance of these two major sources for the neutrons may differ somewhat from that suggested in this discussion.

A situation similar to the Canadian pitchblende exists in the cases of the other pitchblende ores having a greater uranium content. More neutrons are available from spontaneous fission of the uranium and the $(\alpha,n)$ reactions, but the high uranium content of the ore absorbs them, so the plutonium to uranium ratio remains essentially constant. It should be mentioned that when an appreciable fraction of the neutrons is absorbed by uranium, the additional neutrons which result from the fission of $^{235}\text{U}$ contribute significantly to the production of $^{239}\text{Pu}$.

Somewhat different considerations seem to apply in the cases of the monazite ores. In view of the smaller concentration of uranium in monazite, the ratio of $^{239}\text{Pu}$ to uranium in monazite might be expected to be definitely smaller than the ratio in pitchblende if a major source of neutrons were still the spontaneous fission of $^{238}\text{U}$, since the relatively large amounts of elements other than uranium in the ore would capture neutrons, leaving a smaller proportion of neutrons available for capture by the $^{238}\text{U}$. Neutrons due to the spontaneous fission of thorium would not compensate for this effect since the spontaneous fission rate of thorium is smaller than that of uranium by a

factor of $10^5$ or more. However, the contribution of neutrons from $(\alpha, n)$ reactions is relatively more important. The $\alpha$ particles emitted in the decay of thorium and its daughters will give rise to $(\alpha, n)$ reactions with nuclei of the light elements in the same manner as the $\alpha$ particles from the uranium decay chains. One gram of thorium and its decay products will produce $1.5 \times 10^6$ $\alpha$ particles per minute capable of producing neutrons in this manner. Thus, for example, a 100-g. sample of a typical monazite which contains 6.5% thorium, 1.6% uranium and light elements in about the same abundance as in the pitchblende used in the previous example, will emit about two neutrons per minute due to spontaneous fission and about five or ten neutrons per minute due to $(\alpha, n)$ reactions. In order to maintain the $\text{Pu}^{239}$ to uranium ratio seen in North Carolina monazite, about 0.4 neutrons per minute must be captured by the uranium. If just the uranium and thorium competed for the neutron capture, the uranium in the ore would capture somewhat less than half of those available. Monazite ore, however, contains an appreciable amount of the rare earth elements, which capture neutrons with appreciable cross sections, so that the low fraction of the available neutrons captured by the uranium is reasonable. As the ratio of uranium to thorium in the thorium ores decreases, the number of neutrons obtained from $(\alpha, n)$ reactions becomes even more an important factor. Thus the number of neutrons produced in the ore per gram of uranium is greater in the case of the monazite ores than in the cases of the pitchblende ores, this effect somewhat compensating for the number of neutrons captured by nuclei other than $\text{U}^{238}$ in the monazite ores.

Since these explanations for the source of the plutonium in ores suggest that the presence of large amounts of neutrons absorbing impurities, together with small amounts of uranium (or thorium), should reduce the ratio of $\text{Pu}^{239}$ to uranium, the fergusonite and carnotite ores were investigated in order to test these suggestions further. Carnotite is a potassium uranyl vanadate, while fergusonite is a niobate and tantalate of the rare earth elements with a small amount of uranium. In carnotite, the large amounts of potassium and vanadium would be expected to capture most of the available neutrons. Tantalum, having a high neutron absorption cross section, would be expected to capture most of the neutrons available in fergusonite. In the case of the carnotite ore, the ratio of $\text{Pu}^{239}$ to uranium present was set at $0.4 \times 10^{-12}$ and this should probably be considered to be an upper limit.
This is a factor of ten to thirty below the ratio found in the pitchblends and monazites. Garner, Bonner and Seaborg, working with a five-kilogram sample of ore, reported one part Pu$^{239}$ per $10^{14}$ parts carnotite ore. On the assumption of the same uranium content, this puts the value of the ratio of Pu$^{239}$ to uranium in carnotite below the value of the ratios in pitchblende and monazite by a factor of forty to one hundred. Thus it can be seen that the presence in the ore of elements with high neutron absorption cross sections tends to decrease the amount of Pu$^{239}$ present relative to the uranium content. Of the neutrons available in the ore, a smaller fraction can be utilized for the production of Pu$^{239}$. In the case of the fergusonite ore, less than 0.01 α particle per minute due to Pu$^{239}$ was seen, this being the lower limit of detection in this experiment. Unfortunately, this lower limit corresponds to the same order of magnitude as the Pu$^{239}$ contents of the pitchblende and monazite ores investigated. With larger samples of fergusonite, a better limit could be set. This concludes our quotation from Levine and Seaborg.

The 4n+1 Series in Nature. Except for minute traces of Np$^{237}$ and U$^{233}$ produced continuously by reactions of natural neutrons the 4n+1 radioactive series is missing in nature and our knowledge of the properties of the isotopes making up the series is derived from studies of artificially synthesized materials, as is discussed in Chapter 7.

It was pointed out by Seaborg that uranium-bearing ores should contain trace quantities of Np$^{237}$ formed by the U$^{238}$(n,2n)U$^{237}$→Np$^{237}$ reaction; and it has been suggested by Garner, Bonner and Seaborg that uranium-bearing ores containing an appreciable relative quantity of thorium should contain some long-lived U$^{233}$ formed as the result of the Th$^{232}$(n,γ)Th$^{233}$$^\beta$→U$^{233}$ reaction.

Peppard and co-workers have isolated minute amounts of Np$^{237}$ from aqueous waste concentrates from the processing of many tons of Belgian Congo pitchblende. This neptunium was identified chemically and by determination of its alpha particle energy. These workers also established that the thorium fraction from this concentrate contained Th$^{229}$ in minute amount. This thorium fraction was 10.6% I$^{230}$ and 89.4% Th$^{232}$. The amount of Th$^{229}$ found in this sample relative to Th$^{232}$ was $(4.0 \pm 0.6) \times 10^{-11}$ so that this very small

amount could be detected and measured only by isolation and identification of the 10-day Ac\(^{225}\) daughter. It can be assumed that the Th\(^{229}\) present in the thorium was derived from U\(^{233}\) in the original pitchblende, the decay sequence being the following:

\[
\begin{align*}
U^{233} & \xrightarrow{\alpha} Th^{229} \quad 1.6 \times 10^5 \text{ yr} \\
& \xrightarrow{\alpha} Ac^{225} \quad 7340 \text{ yr} \\
& \xrightarrow{\alpha} \quad 10.0 \text{ days}
\end{align*}
\]

The calculated ratio of U\(^{233}\) to U\(^{238}\) in the pitchblende is \((1.3 \pm 0.2) \times 10^{-13}\). PEPPARD and CO-WORKERS\(^{228}\) believe that most of this U\(^{233}\) was contributed by the Th\(^{232}(n,\gamma)Th^{233} \xrightarrow{\beta^-} U^{233}\) route and that only a small fraction is derived from the decay of Np\(^{237}\) produced via the U\(^{238}(n,2n)U^{237} \xrightarrow{\beta^-} Np^{237}\) route. If all the U\(^{233}\) is, in fact, derived from Np\(^{237}\) decay then one can set an upper limit of \((1.8 \pm 0.4) \times 10^{-12}\) for the Np\(^{237}\) to U\(^{238}\) mass ratio in the pitchblende deposit. The amount of Np\(^{237}\) is considerably less than the amount of Pu\(^{239}\) in the same mineral. The neutrons necessary for the production of Np\(^{237}\) or U\(^{233}\) in mineral samples are derived from the same reactions discussed above in accounting for the natural occurrence of plutonium.

PEPPARD ET AL. examined thorium obtained from monazite for evidence of Th\(^{229}\). They found none and could set an upper limit of \(7 \times 10^{-13}\) for the U\(^{233}\) to Th\(^{232}\) mass ratio in the monazite ore. It is reasonable that the U\(^{233}\) content of the monazite ore be so much less than the pitchblende since the uranium content of the former (0.1%) is so much lower than the latter (45.3%).

Other Induced Natural Activities. No other transuranium element isotopes have been observed in nature although it is apparent that other substances which can be formed through a neutron-induced reaction in uranium and thorium minerals can be found by sufficiently diligent search. Similarly, products of the spontaneous fission process can and have been found. The stable end products of the fission product decay chains are particularly likely candidates for detection since these have been accumulating since the ore was laid down. The identification of such spontaneous fission products in uranium minerals is discussed in Chapter 11.

Unlikelihood of the Existence on Earth of Traces of a Primordial Stock of any Transuranium Element. Consideration has been given to the possibility that the half-lives of some of the transuranium nuclides might be
just long enough that a diligent search in the proper minerals might reveal
the present day existence of slight traces of a primordial stock of these
nuclides. However, as the chart of the nuclides has been filled in and as
more accurate information has been obtained on the half-lives of the border-
line cases it has become clear that there is very little likelihood that any
such traces will ever be found. From an examination of all the half-life
measurements and nuclear stability trends which are reviewed in Chapter 9, we
reach the conclusion that Pu$^{244}$ and Cm$^{247}$ are the longest-lived of the trans-
uranium nuclides. But DIAMOND and BARNES report a value of only $(7.6 \pm 0.2)$
$\times 10^7$ years for the half-life of Pu$^{244}$. If the primeval abundance of Pu$^{244}$
was equivalent to that of Th$^{232}$, and if the elements were formed only 5.5
billion years ago, the present day ratio of Th$^{232}$ to Pu$^{244}$ in thorium ores
must be $10^{22}$. If more reasonable choices of the relative primeval abundances
and of the date of the last element forming process are taken, the ratio of
Th$^{232}$ to Pu$^{244}$ is orders of magnitude greater. Hence, it does not seem pos-
sible that present day amounts of Pu$^{244}$ exceed the limits of detectability.

A lower limit of $4 \times 10^7$ years has been set for the half-life of Cm$^{247}$
by DIAMOND, FRIEDMAN, GINDLER and BARNES. These authors calculate that
if the limit of detection of curium in nature is one atom per $10^{15}$ atoms of
rare earth, and if the abundance of Cm$^{247}$ at a time about five billion years
ago was one atom per 1000 atoms of rare earth atoms, then Cm$^{247}$ could not be
detected if its half-life is less than $1.3 \times 10^8$ years. Because Cm$^{247}$ pro-
duces U$^{235}$ in the course of its chain of descendent activities it is possible
that evidence for the past terrestrial existence of Cm$^{247}$ might be revealed
by an abnormal U$^{235}$/U$^{238}$ ratio in certain minerals. If the time between
the formation of Cm$^{247}$ and the separation of curium and uranium into separable
mineral phases were less than seven time the Cm$^{247}$ half-life, an identifiable
increase (2%) in the U$^{235}$/U$^{238}$ ratio would be found in rare earth minerals
having a rare earth to uranium ratio of 1000 or more.

279. H. Diamond and R.F. Barnes, Phys. Rev. 101, 1064 (1956); see also the
280. H. Diamond, A.M. Friedman, J.E. Gindler and P.R. Fields, Phys. Rev. 105,
679 (1957).
KOHMAN\textsuperscript{281} uses the term \textit{extinct natural radioactivity} to refer to nuclides whose half-lives are too short for the nuclides to have survived in detectable amount, but nevertheless long enough for their decay to have produced effects in nature which can be identified at the present time. He has written an extensive review of this topic. The nuclides, Pu\textsuperscript{244} and Cm\textsuperscript{247}, may fall into this category.

There has been some speculation in the literature\textsuperscript{279,280,282} that the extinct activities U\textsuperscript{236}, Pu\textsuperscript{244} and Cm\textsuperscript{247} have contributed importantly to the radioactive heating of the earth and other objects during the early history of the solar system. It requires a detailed consideration of the possible element forming processes, the time scale for element formation, the time scale for the condensation of matter into sizeable objects and of other cosmological questions before a proper evaluation of this suggestion can be made. We refer the reader to an article by KOHMAN\textsuperscript{283} who concludes that it is unlikely that U\textsuperscript{236}, Pu\textsuperscript{244} or Cm\textsuperscript{247} ever contributed importantly to the treating of the earth compared to U\textsuperscript{238}, U\textsuperscript{235}, Th\textsuperscript{232} and K\textsuperscript{40}.  

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