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**AN INTRODUCTION TO THE
CHEMISTRY OF RADIO-ACTIVE
SUBSTANCES**

AN
INTRODUCTION TO THE
CHEMISTRY OF RADIO-
ACTIVE SUBSTANCES

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PREFACE

IN writing this book I have tried to bring before students who are interested in radio-activity the chief facts concerning the chemistry of radio-active substances at present known. As far as I am aware there is no book in English on this subject which is reasonably up-to-date.

This book is not a monograph in the ordinary sense, and although I have taken pains to collect together the best and most recent data and views on the subject, I have made no attempt to deal with any part of it exhaustively, and I have not thought it necessary to cite authorities and references except for a few statements. A monograph very rightly, I think, should give chapter and verse for every statement of importance, but a book like this one, which does not pretend to do more than give a short account of a large subject, need not. Below are given a list of books which I recommend as primary sources of information on radio-activity and cognate subjects, and from them, merely by consulting their indexes, a reader may speedily be put on the track of the original papers dealing with any matter on which he requires further information.

I wish to express here my indebtedness to the writers of these books in the task of compiling my own.

The following is the list :

- (1) Sir ERNEST RUTHERFORD, F.R.S. : *Radio-active Substances and Their Radiations*. (Cambridge University Press, 1913.)

This is the standard book on radio-activity in English, and contains the whole of the information on which the chemical side is based. It deals exhaustively and in a masterly way with work on radio-activity, both chemical and physical, to the end of the year 1912.

- (2) Dr. S. MEYER and Dr. E. v. SCHWEIDLER : *Radioaktivität*. (Leipzig, 1916.)

This work in German is on the same general lines as Sir E. Rutherford's book, but includes the important information obtained between 1912 and 1916, when the chemistry of the radio-elements underwent great development.

- (3) Prof. FREDERICK SODDY, F.R.S. : *The Chemistry of the Radio-Elements*. (Longmans, 1915.)

This book deals with the chemical side of the subject, with full references of work done up to 1915. It is at present out of print.

- (4) Dr. K. FAJANS : *Radioaktivität*. Third edition. (Vieweg, Braunschweig, 1921.)

This is an excellent summary of the latest work on radio-activity in German. It deals particularly with isotopes and the new ideas on the chemical elements developed by recent work on radio-activity and on the structure of the atom. It covers a wide

field, but it is too short to serve as a textbook. It gives references to all recent work.

- (5) *Annual Reports of the Progress of Chemistry*. The four volumes for 1914, 1916, 1918, and 1920, issued by The Chemical Society (Gurney and Jackson).

The sections on Radio-activity are by Prof. Soddy and summarise the work done in the year of and the year before publication. They give, also, full references to the original papers.

- (6) Dr. J. N. FRIEND : *A Textbook of Inorganic Chemistry*. Nine vols. (Griffin, 1918-21.)

This is a book of reference on inorganic chemistry. Vol. I deals, *inter alia*, with the periodic system, X-ray spectra, and radium emanation ; Vol. III with radium and its products ; Vol. IV with actinium and the actinium series ; Vol. V with thorium and the thorium series ; Vol. VII with uranium and the uranium series. Full lists of authorities are given. (Vol. III and Vol. VII are not yet published.)

- (7) E. CAHEN and W. O. WOOTTON : *The Mineralogy of the Rarer Metals*. (Griffin, 1920.)

This work describes radio-active minerals.

A. S. RUSSELL.

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AN INTRODUCTION TO THE CHEMISTRY OF RADIO-ACTIVE SUBSTANCES

CHAPTER I

THE SOURCES OF THE RADIO-ELEMENTS

Introduction.—The name “radio-active” is applied to a class of bodies like uranium, thorium, radium, and their compounds which possess the property of spontaneously emitting radiations of different kinds capable of passing through substances which are opaque to ordinary light. The characteristics of these radiations are their powers (1) of penetration, (2) of ionising gases, and consequently of discharging charged bodies like the leaf-system of an electroscope, (3) of affecting a covered photographic plate, and, when sufficiently powerful, (4) of producing fluorescence on screens of suitable material. The property is spontaneous, *i.e.* it cannot be initiated, stopped, accelerated, or retarded; it is atomic; it is an accompaniment of the transformation of an atom into an atom of another kind. A brief definition of a “radio-active substance” is, “one whose atoms emit spontaneously α - or β -particles.” Such atoms are said to break up or to disintegrate or to be transformed. •

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Because radio-activity is an atomic property it is customary to refer to and to think of a radio-active substance as an element even when actually it is a compound, and the term "radio-element" will often be used in this sense in the pages that follow.

The radio-elements include some forty elements possessing atomic weights which lie between 206 and 238.2. Above the limit of 209 there are no elements which are *not* radio-active. It would thus appear that there is a connection between high atomic weight, *i.e.* complexity of atomic structure, and radio-activity, a view borne out by other work in physics. Two elements of low atomic weight, however, rubidium and potassium, are also radio-active in a small but perfectly definite way. These alone of elements possessing atomic weights of less than 206 have so far been shown to possess radio-activity.

Of the radio-elements two alone, uranium and thorium, were known before the discovery of radio-activity in 1896, and these are still the only ones which may be purchased in weighable quantities at a reasonable cost. The remainder exist in small amount only, some being measured in grams, others in fractions of a milligram, and the majority in altogether unweighable quantities. Nevertheless, it has been found experimentally that each of these forty radio-elements is a perfectly genuine element in the chemical sense with characteristic physical and chemical properties. The *additional* property of radio-activity enables these substances to be recognised unmistakably no matter what chemical operations they have been subjected to, and at concentrations far less in amount than can

be detected by the most sensitive spectroscope. What appears to be a hopeless task, namely the investigation of the chemical properties of bodies most of which exist in very small quantities, is for this reason quite practicable. The chemistry of nearly every radio-element has now been experimentally investigated and is accurately known.

It will be shown in the sequel that every radio-element with the exception of rubidium and potassium is connected genetically either with uranium or with thorium, the two radio-elements to be first discovered. It follows, therefore, that the radio-elements are found in minerals which contain uranium and thorium, and there alone.

Minerals containing uranium.—Uranium is found combined in a few rare minerals, the most abundant of which are carnotite, pitchblende, autunite, bröggerite, cleveite, thorianite, and thorite.

(a) *Carnotite* is a hydrated vanadate of potassium and uranium, $K_2O \cdot 2UO_2 \cdot V_2O_5 \cdot 3H_2O$, occurring as a secondary mineral impregnating a porous, sedimentary sandstone; a yellow crystalline powder found chiefly in Colorado and Utah.

(b) *Uraninite*, or *pitchblende*, is U_3O_8 (or UO_2 and UO_3 in varying proportions), with PbO , Fe_2O_3 , and traces of ThO_2 and rare earths. It occurs primary as a constituent of rocks, and secondary in veins with metaliferous sulphides. It is black in colour. Its chief sources are Bohemia, Saxony, Colorado, East Africa, and Cornwall.

(c) *Autunite* is a hydrated phosphate of calcium and uranium, $Ca(UO_2)_2(PO_4)_2 \cdot 8H_2O$. It is probably

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an alteration product of other uranium minerals. It is yellow and greenish-yellow in colour. The chief sources are Portugal, U.S.A., and South Australia.

(d) *Bröggerite* resembles uraninite in many respects, but contains thorium.

(e) *Cleveite* is a hydrate of uranium, lead, thorium, yttrium, and other rare earths. It occurs in Norway.

(f) *Thorianite* and *thorite*.—See under Thorium Minerals.

The composition of the principal minerals may be sufficiently indicated by the typical analyses tabulated in Table 1.

TABLE 1

<i>Constituent.</i>	<i>Carnotite.</i>	<i>Pitchblende.</i>	<i>Autunite.</i>
U_3O_8 . .	47·8	82·63	61·34
V_2O_5 . .	16·8	—	—
Fe_2O_3 . .	19·4	3·21	—
Al_2O_3 . .	5·7	0·40	—
CaO . .	1·0	1·00	5·24
PbO . .	1·3	6·39	traces
K_2O . .	5·2	—	—
Na_2O . .	1·8	0·31	—
P_2O_5 . .	—	0·06	14·97
SiO_2 . .	—	2·67	—
Water . .	—	3·17	19·66

Minerals containing thorium.—The chief sources of thorium are the minerals monazite sand, thorite, orangite, and thorianite.

(a) *Monazite sand*.—Monazite is essentially an orthophosphate of the cerium group of rare earth elements, containing nearly always some thorium. This mineral is a constituent of beach sand, occurring there in small

yellow brittle grains. The most abundant sources are the coast of Brazil and Travancore in Southern India.

(b) *Thorite* is an altered form of an original thorium silicate, and is ThSiO_4 with up to 7% Ce_2O_3 and up to 10% UO_3 . It occurs in various parts of Norway, Ceylon, and in New York State. It is a primary constituent of pegmatite dikes, and is black in colour.

(c) *Orangite* is another altered form of an original thorium silicate.

(d) *Thorianite* consists of oxides of thorium (50 to 70%), of uranium (10 to 30%), and of lead (2 to 5%), with oxides of cerium, zirconium, and rare earths (0.1 to 10%). It occurs as a primary constituent of pegmatite dikes in hard black cubic crystals in Ceylon and Madagascar. Its geological age is probably Archean. It is an excellent source of all radio-active elements.

Typical analyses of these minerals are given in Table 2.

TABLE 2

<i>Constituent.</i>	<i>Monazite Sand.</i>	<i>Thorite.</i>	<i>Thorianite.</i>	
ThO_2 . .	5.00	71.8	63.36	79.25
U_3O_8 . .	—	1.25	28.00	15.25
PbO . .	—	—	2.90	2.6
Ce_2O_3 and rare earths . .	63.75	2.10	1.16	1.0
Fe_2O_3 . .	3.00	3.55	1.27	0.55
CaO . .	0.15	—	0.85	1.15
SiO_2 . .	1.20	13.55	0.77	0.2
P_2O_5 . .	26.30	1.8	—	—
Ignition loss .	0.25	5.85	1.32	—

These two sets of minerals are sources of all the radio-elements.

CHAPTER II

THE BEGINNINGS OF RADIO-ACTIVITY AND THE DISINTEGRATION THEORY

“THE subject of radio-activity belongs to the borderland of chemistry and physics.” Both have been indispensable in its development, though without doubt physics has been the more important. It follows, therefore, that, for a proper understanding of the chemical side of the subject, with which alone this book professes to deal, some knowledge of the more relevant physical phenomena of the subject must be possessed. The chemical and the physical sides are at times so interdependent that it is not feasible to deal fully with the physical phenomena in a preliminary chapter preparatory to a description of the chemical side. A short description of the main physical facts of the subject, superficial though it is, must be interwoven with that dealing purely with the chemistry of the radio-elements, even if the author were purposely to ignore the historical development of the subject and merely to confine himself to stating the facts as they are known at present.

It is convenient, however, in describing the subject, to deal with it to some degree historically, and the main points in the history of the chemical side are for convenience summarised below. Each will be treated in some detail in the sections which follow.

Summary of the historical development of the subject.—(a) Discovery of the radio-activity of uranium by Becquerel (1896), and of thorium by Mme Curie and by Schmidt (1898).

(b) Discovery that radio-activity is an atomic phenomenon and may be detected by its

(1) photographic action ;

(2) its power of ionising gases ;

(3) its fluorescent action on prepared screens.

Isolation of four new elements, polonium and radium by the Curies (1898), actinium and radio-lead.

(c) The experiments on the radio-activity of thorium and of uranium which led to the disintegration theory of the cause of radio-activity (Rutherford and Soddy, 1902–3). Discovery of more radio-elements and the gradual elucidation of the three disintegration series from 1904 onwards.

(d) The theory of the structure of the atom (Rutherford 1911, and other workers later).

(e) The experiments leading to the idea of atomic number ; showing that atomic number, not atomic weight, is the fundamental property of an element ; that the chemical properties of the elements are a periodic function of their *atomic numbers* (Moseley, 1912–13).

(f) The theory and the experimental proof of the existence of isotopes of radio-elements. The relation of the radio-elements to the periodic system. (Marckwald, 1909 ; Fajans, Russell, Fleck, Soddy, 1913.)

Discovery of radio-activity.—The discovery of X-rays by Röntgen, of Munich, towards the end of the year 1895 was the beginning of a new epoch in modern

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physics. It attracted great public as well as scientific interest, an interest that has grown as the subject has been developed in the last twenty-five years. X-rays were shown to have the power of passing through thin layers of bodies, whether opaque or not to ordinary light, being absorbed roughly in direct proportion to the density of the material they traversed. They had the property of ionising gases, and so of discharging charged bodies like the leaf-system of an electroscope; they affected a covered photographic plate; they produced fluorescence on screens of suitable material.

In following up this discovery in 1896, Becquerel, of Paris, connected the phenomena with phosphorescence, and tried the action of a number of fluorescent and phosphorescent substances upon the photographic plate. His results were negative until he tried the salts of uranium. He found that the salts of uranium with which he experimented, whether they exhibited phosphorescence or not, and equally whether kept in daylight or the dark, affected a covered photographic plate. It was at once realised that this was a new property of uranium, and one unconnected with phosphorescence; it was called radio-activity.

The radiations from uranium and its compounds were found to resemble X-rays in ionising gases, in affecting a photographic plate, and in producing fluorescence on suitable screens, but they differed in that they were given forth spontaneously and were unaffected by any change of conditions. A systematic examination of minerals and preparations were then undertaken by several workers to see what other substances exhibited the new property. The procedure

usually was to place the mineral or preparation on top of a covered photographic plate for hours or days, and then see if the plate on development showed an effect. Results were negative except for compounds of thorium, which were shown in 1898 independently by Mme Curie and G. C. Schmidt to be radio-active like uranium.

Radio-activity an atomic phenomenon.—The next thing to be proved was important. Radio-activity was shown to be an *atomic* phenomenon. When uranium or thorium compounds (but not minerals) were examined, the radio-activity, determined usually by the amount of ionisation produced in a gas, was found to be proportional to the amount of uranium and thorium present calculated as elements, and independent of the other elements composing the compound. The fact that the property was atomic was not only very interesting theoretically, but it led in subsequent chemical works to great simplification, and to the isolation of new radio-active bodies, for since a radio-active body is always radio-active, whatever compound it forms, it can never escape detection by its radio-activity at any stage of the chemical processes through which it is put.

Polonium and radium.—Mme Curie compared the activities of uranium and thorium minerals with uranium and thorium compounds, and made the important and unexpected observation that several minerals containing uranium were more radio-active than they would have been had they lacked impurities and been composed of uranium alone. She prepared artificially several minerals, and these had, as was

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expected, merely the amount of radio-activity that was calculated from their composition, and consequently had less than the natural ones. Some of her results are given in Table 3.

TABLE 3.—RELATIVE RADIO-ACTIVITY OF URANIUM MINERALS AND COMPOUNDS

		<i>Compound.</i>	<i>Activity in arbitrary units.</i>
Natural Minerals	{	Pitchblende . . .	3.1
		Chalcolite . . .	2.3
		Autunite . . .	1.2
		Carnotite . . .	2.7
		Uranium . . .	1.0
Artificial Minerals	{	Uranium and Potassium sulphate . . .	0.3
		Artificial chalcolite . . .	0.4

Similar results were obtained with thorium minerals.

Since the radio-activity of a compound was proven independent of the composition, and dependent only on the amount of uranium in it, the relative activity of minerals should be less than that of uranium. The expected result was shown in the artificially prepared minerals, but not in the natural ones. To explain this Mme Curie put forward a very concrete explanation, namely, that in these natural minerals were small quantities of an element or of elements having a greater radio-activity than uranium and undetected by ordinary analysis—in other words, new radio-elements. This theory was verified experimentally. Starting with pitchblende (a uranium mineral containing oxides

of uranium, lead, iron, with traces of calcium, barium, bismuth, thorium, and rare earths) M. and Mme Curie made a full qualitative analysis of it in the ordinary way and examined carefully each precipitate for radio-activity by physical methods. Along with the bismuth, an impurity in the mineral, a very radio-active substance which they called polonium was separated. This substance appeared to be chemically radio-active bismuth, but it was clearly not bismuth, for bismuth is not radio-active; besides, it could be separated to some extent from it. It was consequently a new substance.

They also found that the precipitate of barium, another impurity in the mineral, contained a highly active substance which was, at first partially, and later entirely, separated from the non-radio-active barium by a series of fractional crystallisations. This also was without doubt a new radio-active substance, and was named radium.

Polonium and radium, even when associated with the inactive substances with which they were separated, were weight for weight many thousands of times more radio-active than uranium.

Actinium and radio-lead.—In 1900, by adopting the methods of the Curies, Debierne separated a third radio-active substance with the iron group which was called actinium. Associated with the lead of the mineral was found in a similar way by Hofmann and Strauss in 1901 a fourth radio-active substance then named radio-lead. At this stage, then, there were six radio-active substances known, uranium and thorium, polonium which associated with bismuth, radium

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with barium, actinium with iron, and radio-lead with lead.

The discovery of radium created the greatest scientific interest, and led to some extravagant talk with regard to its properties. When sufficiently concentrated from barium it showed to an extraordinary degree the properties of a radio-active body in ionising gases, affecting a photographic plate, and producing luminescence on a screen. Its two most obvious properties, arising from its emission of energy, were that it glowed in the dark, and that it kept itself above the temperature of surrounding objects. This constant emission of light- and heat-energy in all circumstances, without any noticeable diminution over a period of years, created general surprise and great interest, because it apparently contradicted the law of the conservation of energy, and showed the existence of a perpetual-motion machine. One gram of radium, with its products in equilibrium, calculated as element, evolves continuously about 130 gram-calories per hour.

Excited activity.—There was another set of observations difficult to explain. It was found that *all* bodies placed in the neighbourhood of compounds of thorium, actinium, and radium, but not of uranium, became apparently radio-active. The names given for this phenomenon, “the excited activity” and “the induced activity,” reveal the basic ideas of its cause then in the minds of those who were investigating it. The activity excited in a non-radio-active body lacked the permanency of that of the compounds exciting it; also it varied in nature and amount apparently capriciously. It received a simple explanation in due

course, but so long as the idea was prevalent that radio-activity could be induced in ordinary materials by radio-active substances, difficulties in the way of progress seemed very great.

The disintegration theory of Rutherford and Soddy.—There was yet no satisfactory theory to account for these phenomena. The one or two hypotheses that had been put forward neither explained things simply nor suggested further experiments.

A great advance in the subject and a clear explanation of the difficulties was given in 1902-3 by Rutherford and Soddy, as a result of a happy continuation of physical and chemical work on preparations of thorium. This subject will be dealt with in detail in the next chapter. Preparations of thorium, actinium, and radium had been found to generate continuously emanations which gave rise to the "excited" activity of bodies in their neighbourhood. Rutherford and Soddy showed that the producer of the emanation given off by thorium preparations was not thorium itself, but a very minute impurity which could be separated from the thorium by a simple chemical operation. It was called thorium X because of its mysterious character. Thorium X produced the emanation and the "excited" activity; thorium did not. Thorium X, however, was not permanent; it lost its radio-activity with time, while the thorium initially freed from thorium X spontaneously produced a new supply. They concluded that with a given quantity of a preparation of thorium there was associated a definite but exceedingly minute amount of thorium X. This amount could neither be increased

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nor decreased. The thorium X might be removed from the thorium chemically when it spontaneously decayed, but as much as decayed in any given time was found to be grown in the thorium preparation, so that on adding the two portions the original amount was reached. If the thorium X is not removed from the thorium the two processes, growth from thorium and decay into something else, proceed simultaneously so that the amount of thorium X remains constant.

In order to explain the results observed, Rutherford and Soddy put forward a very definite and concrete explanation called the disintegration theory, which offered a quantitative explanation of the experimental facts and suggested many new lines of experimental work.

According to this theory radio-activity is due to the expulsion of material particles at a great speed from atoms which explode spontaneously with intense violence. In a radio-active body a fraction only explodes in this way in a small interval of time. The particles shot out (we now know) are of two kinds, one with a mass approximately four times that of the hydrogen atom, bearing two positive charges of electricity, with a velocity of about a tenth of that of light, and consequently with great energy; the other, of less energy, a single negative charge of electricity, with a velocity nearly that of light, but with almost negligible mass. These material particles are parts of the atom which have exploded; as a consequence the atom remaining after the explosion is different from the atom before, *i.e.* different from an atom that has not exploded. In a radio-active change, then, one kind

of atoms is spontaneously being transformed into another with the liberation of energy; both bodies are distinct chemical elements with characteristic chemical properties and capable of being separated by the methods of analytical chemistry. If the second body is itself radio-active, it will be partially transformed into a third, and the third, if radio-active, into a fourth, and so on until a body is reached which is not radio-active. A radio-active body consequently may contain several other radio-active bodies which are connected with the parent body by the relation father, son, grandson, great-grandson, etc. Much of the chemistry of the radio-elements is devoted to separating these products genetically connected with one another.

The rate at which the process of disintegration proceeds in any radio-element was found to be constant, but very different for different radio-elements. This is one reason why a body like radium is so radio-active compared with uranium.

The principle of the conservation of energy was not violated. The long-continued emission of energy which gave the surprising results shown most clearly by radium was derived, on this theory, from the internal energy of the atom. The internal energy of an atom was surprisingly great in amount (indeed, this is one of the most remarkable discoveries in radio-activity), but there was nothing abnormal in this fact. The energy released on disintegration is simply the difference in internal energies of the original atoms and the resultant atoms. Moreover, the emission of energy by any particular body, although continuous,

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decreased continuously in amount, but often so slowly as apparently to appear not to do so, for clearly for every atom disintegrated there is one atom the less of the body disintegrating. The disintegration theory received further support in 1903 by the remarkable observation of Ramsay and Soddy that helium was produced from radium emanation. It was further shown that the "induced" or "excited" activity was a non-gaseous type of matter itself radio-active, the product of disintegration of the gaseous emanations.

CHAPTER III

THE DISINTEGRATION THEORY

THE disintegration theory of radio-activity mentioned in its historical setting in the last chapter will now be described in detail. The view of Rutherford and Soddy is that radio-activity is due to an explosion of intense violence which results from the transformation of an atom of a radio-element into a completely different atom. In the explosion a portion of the atom being transformed is expelled with a very great velocity. The process is spontaneous and continuous. It is now known that the seat of the transformation (or disintegration) in the atom is the nucleus, but the reason for the disintegration of the nucleus is not yet known. In a given interval of time a definite fraction of the whole number of atoms of the radio-element explode. Before the moment of explosion it is impossible to distinguish in any way between an atom about to explode and one which does not; after explosions the disintegrated atoms have different chemical properties, and may be separated readily from the parent body by the ordinary methods of qualitative analysis as soon as its chemical reactions are known. Uranium atoms, for example, disintegrate with the expulsion of α -particles. The resultant body (known as uranium X_1) has an atomic weight of

$238 - 4 = 234$, and may be separated quantitatively from uranium by taking advantage of its similarity to thorium. Thorium is most conveniently separated from uranium by precipitating it from a neutral solution with *m*-nitrobenzoic acid. To separate uranium X_1 from uranium, therefore, a little thorium nitrate is added to the solution prior to the precipitation with *m*-nitrobenzoic acid, when the precipitated thorium carries down with it the whole of the uranium X_1 . If uranium X_1 existed in sufficient amount to allow of filtration, it would not be necessary to add the thorium to act as a nucleus for it.

The definite fraction of the atoms which explode in a given interval of time, *i.e.* the rate of disintegration, is a constant independent of all known factors. As the phenomenon is atomic, the rate is not affected by the combination of radio-active atoms with other atoms. For example, the rate of disintegration of radium bromide, radium sulphate, and of metallic radium are identical. Again, the disintegration of atoms cannot be initiated or stopped, nor can the rate of disintegration be affected in any way by such influences as concentration of radio-active substances, changes of pressure or of temperature. For example, a gram of radium disintegrates at the same rate as 10^{-12} grams. Further, radium in a mineral, or in a laboratory preparation, or in the blast furnace (so long as none of the material is actually lost), in a vacuum, or at a pressure of a thousand atmospheres, disintegrates at exactly the same rate. This rate, the nature of the radiation expelled, and the velocity of expulsion of the radiation, are characteristics of each

radio-element. The second and third of these will be dealt with before the first.

Types of radiation.—The radiations emitted by radio-active substances are grouped under three heads :

(a) *The α -particle.*—This is the least penetrating of the three types of radiation. It carries two charges of positive electricity, has a mass of 4.00 (oxygen = 16), and is really a charged atom of helium. It is expelled by different radio-elements with different velocities, all of which are of the order of one-twentieth of the velocity of light. It corresponds to the positive rays produced in a vacuum tube by an electric discharge.

(b) *The β -particle.*—This is an electron, *i.e.* a particle carrying one charge of negative electricity and having an apparent mass of $\frac{1}{1836}$ of that of a hydrogen atom. β -particles are of the same nature as the cathode rays produced in a vacuum tube. They are usually expelled with velocities from 33% to 99% of that of light. They come off in groups emitted at a definite velocity, so that a pencil of β -particles deflected in a magnetic field shows a magnetic spectrum.

(c) *The γ -ray.*—This, like the X-ray, carries no charge, and is a wave-motion propagated with the velocity of light. It accompanies the emission of a β -particle.

γ -rays are a type of X-rays of much shorter wave length than can be, or are likely to be, produced by laboratory methods.

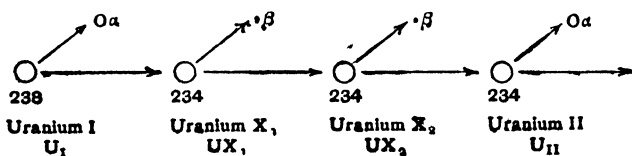
It is the general rule that *either* an α - or a β -particle (but not both) is expelled by a radio-element, and that one particle only is expelled by each atom disintegrating. The expulsion from the nucleus of the charged

α - and β -particle (but not the γ -ray) causes an alteration of the charge on the nucleus, and, as we have considered above, therefore a complete alteration in the properties of the atom which explodes. The whole of these new atoms arising from these explosions form a new element, which exists with the parent element and which can be separated from it by chemical means. This new element, if radio-active, will in turn produce a third element at a rate which is characteristic of itself, the third element, if radio-active, a fourth, and so on, until the n th radio-element in succession is transformed into an inactive element, when the process apparently stops.

An example will make this clear. The atoms of uranium (atomic weight 238) are not permanently stable systems, but on an average about one atom in every 10^{18} becomes unstable and breaks up each second. This atom breaks cleanly into (1) an α -particle which is expelled with great velocity, and (2) the rest of the atom (a new atom) which remains. Since the α -particle is an atom of helium of atomic weight 4, the new atom has decreased in weight by 4 units, *i.e.* its atomic weight is 234. These new atoms constitute a new substance, which has been called uranium X_1 , and their physical and chemical properties resemble those of thorium and are quite distinct from those of uranium. The atoms of uranium X_1 are far more unstable than those of uranium itself, for on an average one in every 10^7 disintegrates per second. The explosion in this atom results in the emission of a β -particle from the nucleus, and a new atom of the same atomic weight as that of uranium X_1

results. There is no measurable change of atomic weight, because of the almost negligible mass of the β -particle, but the charge on the nucleus has been altered, and consequently the resultant atom has different chemical properties. The body composed of these resultant atoms is called uranium X_2 . The atoms of this body are more unstable than those of its parent, uranium X_1 , about one in every hundred disintegrating per second. The particle emitted is a β -particle from the nucleus. The product, therefore, has different chemical properties, but the same atomic weight. It is called uranium II.

These three transformations may be represented graphically thus :



A series of such elements in its entirety is called a disintegration series. Three of these are known, the uranium, the actinium, and the thorium series. A disintegration series commences with what is called a primary radio-element, and is such that every element in it, subsequent to the primary, is the product of the one preceding it, and the parent of the element succeeding.

The heads of these three series, the primary radio-elements, with necessary data are given in Table 4.

TABLE 4

<i>Atomic Number.</i>	<i>Element.</i>	<i>Symbol.</i>	<i>Atomic Weight.</i>
92	Uranium .	U	238.2
91	Protactinium	Pa	230
90	Thorium .	Th	232.2

Decay and growth of a radio-element.—The rate at which a radio-element disintegrates may now be considered. We have seen that this has been found experimentally to be a constant for each element, and is denoted by λ . Every radio-active substance, when freed entirely from its parent substance, is found to decay owing to disintegration according to an exponential law with the time. Let N_0 be the number of atoms of a radio-element present at any time, N the number which remain after a time t later, then the relation is expressed by the equation :

$$\frac{N}{N_0} = e^{-\lambda t} \quad . \quad . \quad . \quad (1)$$

where λ represents the fraction of the total number of atoms which break up per second if t be measured in seconds, or per (any other) unit of time if t also be expressed in that unit. λ is known as the disintegration—or transformation—constant. It varies enormously from element to element. For uranium I, for example, it is 1.4×10^{-10} per year ; for uranium X₁, 0.0282 per day, and for actinium A 350 per second.

It may be deduced from (1) by differentiation that

$$\frac{dN}{dt} = -\lambda N \quad . \quad . \quad . \quad (2)$$

which shows that the number of atoms which break up in unit time is always proportional to the number unchanged at that time.

The usual form in which (1) is expressed so that λ may be calculated from values of N , N_0 , and t determined experimentally is

$$\lambda = \frac{\log N_0 - \log N}{0.4343 t} \quad . \quad . \quad (3)$$

where logarithms are to the base 10.

(3) is obtained from (1) by taking logarithms to base 10 of both sides, and remembering that $\log_{10} e$ is 0.4343.

Although λ is a characteristic constant of a radio-element, the rate of disintegration is nearly always expressed for convenience in terms of two other constants which are very simply connected with λ . These are known as the Half-Value Period (P) and the Period of Average Life (L). These three constants are connected by the equations

$$L = 1.443 P = \frac{1}{\lambda} \quad . \quad . \quad . \quad (4)$$

as will now be shown.

A radio-element disintegrates according to equation (1), which is the equation of a monomolecular reaction.

It is well known that in this reaction there is an interval of time P, which is constant, at the end of which the quantity of material present is half that at the beginning of the interval. This is the important constant, the Half-Value Period, of radio-activity.

$$\begin{aligned}
 \text{From (3)} \quad t &= \frac{\log N_0 - \log N}{0.4343 \lambda} \\
 \text{Put} \quad t &= P \text{ when } N = \frac{1}{2} N_0 \\
 \text{then} \quad P &= \frac{\log 2}{0.4343 \lambda} = \frac{1}{1.443 \lambda} \quad (5)
 \end{aligned}$$

Again, the law of transformation shows that theoretically any atom may exist unchanged for any time from zero to infinity; but the atoms of any one particular radio-element have in mass an average life of so long. It may be calculated that the measure of this PERIOD OF AVERAGE LIFE of the atoms of the radio-element is numerically the reciprocal of λ .

For with the symbols of equation (1), the number of atoms of a radio-element in existence at time t is N , the number which disintegrate per second is λN , the number which disintegrate in time dt is $\lambda N dt$, i.e. $\lambda N_0 e^{-\lambda t} dt$, N_0 being the original number of atoms. As each of these atoms has a life t the average life of the whole number is given by $\frac{1}{N_0} \int_0^\infty \lambda N_0 t e^{-\lambda t} dt$.

This when integrated in the usual way (by parts) comes out to $\frac{1}{\lambda}$ (6)

From equations (5) and (6) we have the equality stated in (4), namely:

$$\begin{aligned}
 \text{Period of Average Life} &= 1.443 \text{ Half-Value Period} \\
 &= \text{Reciprocal of Disintegration} \\
 &\quad \text{Constant} \quad . \quad . \quad (7)
 \end{aligned}$$

The Half-Value Period is the constant most commonly used to indicate the rate of disintegration.

Example.—For uranium X_1 , $\lambda = 0.0282$ per day.

DECAY AND GROWTH OF A RADIO-ELEMENT 25

This is determined experimentally by inserting the necessary data in equation (3) :

$$\text{Period of Average Life} = \frac{1}{0.0282} = 35.5 \text{ days.}$$

$$\text{Half-Value Period} = \frac{35.5}{1.443} = 24.6 \text{ days.}$$

The interpretation of the last constant is as follows :
If we have a quantity of uranium X_1 now, in 24.6

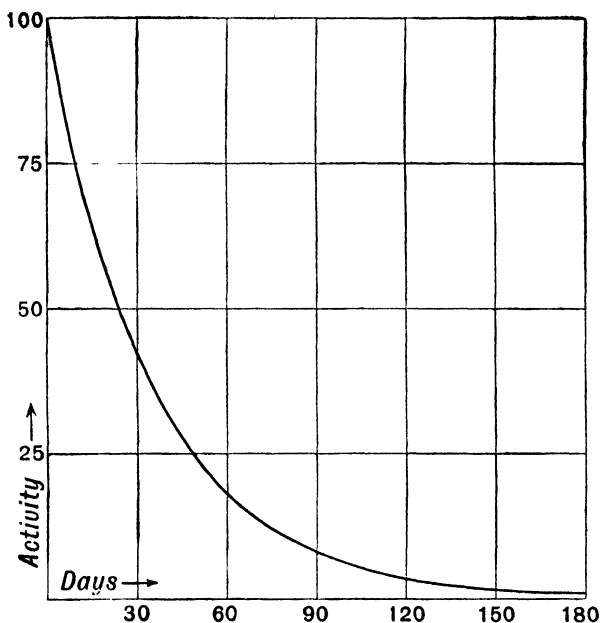


FIG. 1.—THE DECAY CURVE OF URANIUM X_1 .

days half alone remains (the other half has disintegrated), in 49.2 days a quarter remains, in 73.8 days an eighth, in 98.4 days a sixteenth, and so on. The decay curve of this body [the graph of equation (1)] plotting

values of N against values of t , is shown in Fig. 1, the curve falling exponentially to zero. It is more usual (being in practice more accurate) to graph the equation

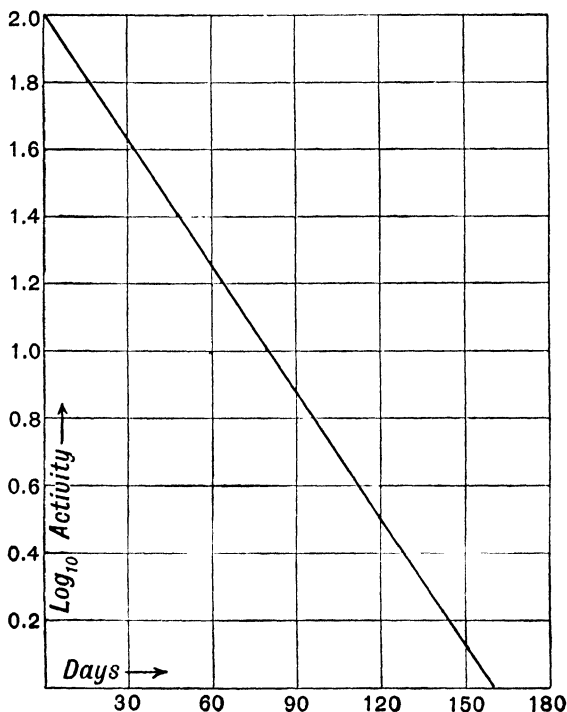


FIG. 2.—THE DECAY CURVE OF URANIUM X_1 PLOTTED LOGARITHMICALLY.

(3), plotting values of $\log N$ against values of t , as shown in Fig. 2. The relation now is a straight line.

Growth of a radio-element.—Consider again the transformation,



If UX_1 were not radio-active, it is clear that it must accumulate with time in a preparation which contained initially U_I only. Since, however, it disintegrates to form UX_2 it does not accumulate, for there comes a time when the number of atoms of UX_1 produced by U_I in a given interval of time is the number disintegrating to form UX_2 . After that time has been reached the quantity of UX_1 remains constant. The *amount* of UX_1 remains constant, but the atoms comprising the material do not remain unchanged, some breaking up into UX_2 , others taking their place from the breaking-up of U_I . The substance is then said to be in equilibrium with its parent substance, and this maximum amount present at equilibrium is called the equilibrium-amount. It follows that if UX_1 be completely separated from U_I chemically, the former will decay as we have seen above, but in the U_I remaining it will grow as fast as it decays until equilibrium is again reached. This growth of the equilibrium-amount of a product in its parent, when represented graphically, is called a rise curve. A rise curve is the complement of a decay curve, its equation being

$$\frac{N}{N_{\infty}} = 1 - e^{-\lambda t} \quad . \quad . \quad . \quad (8)$$

where the symbols have their previous significance, and N_{∞} represents the number of atoms at equilibrium.

The rise and decay curves of uranium X_1 are shown in Fig. 3.

The decay of a product and growth in its parent according to these simple laws holds for all radio-elements whose parents disintegrate slowly.

Radio-active equilibrium.—If $\lambda_1, \lambda_2, \lambda_3, \lambda_4$ be the

disintegration constants, *i.e.* the fractions of the whole which break up per second, of U_I , UX_1 , UX_2 , U_{II} respectively, then when these four elements are in equilibrium (as they are in an old untouched uranium-containing mineral), the number of atoms of U_I break-

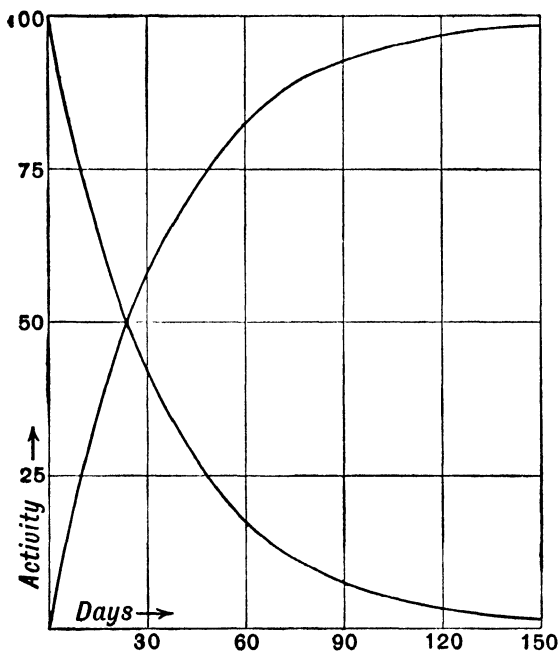


FIG. 3.—THE DECAY- AND RISE-CURVES OF URANIUM X_1 .

ing up per second is equal to that of UX_1 , of UX_2 , and of U_{II} . Expressed mathematically,

$$\lambda_1 A_1 = \lambda_2 A_2 = \lambda_3 A_3 = \lambda_4 A_4 = \text{etc.}$$

where A_1 , A_2 , A_3 , A_4 , are the total number of atoms of the four elements respectively at equilibrium,

$$\begin{aligned}\text{Hence, } A_1 : A_2 : A_3 : A_4 &= \frac{1}{\lambda_1} : \frac{1}{\lambda_2} : \frac{1}{\lambda_3} : \frac{1}{\lambda_4} \\ &= P_1 : P_2 : P_3 : P_4\end{aligned}$$

It follows that at equilibrium the amounts of different radio-elements are proportional to their half-value periods. Knowledge of the half-value periods is therefore very necessary in a study of the chemistry of these bodies, for it enables one to calculate the amounts of different elements in a preparation or a mineral; it gives one an idea of the amount of material one is dealing with in chemical operations, and of the relative permanence of artificial preparations of the element.

Example.—In an old uranium mineral we have all the products of the uranium disintegration series in equilibrium with uranium. The half-value period of uranium is 5×10^9 years, that of uranium X_1 24.6 days, that of radium 1,600 years, that of radium A 3 minutes, and that of radium D 16 years. In a quantity of mineral containing 1 kilo of uranium calculated as element there is therefore

$$\frac{1000 \times 24.6}{5 \times 10^9 \times 365} \text{ of a gram of uranium } X_1, \text{ or } 0.000013 \text{ milligram,}$$

$$\frac{1000 \times 1600}{5 \times 10^9} \text{ of a gram of radium, or } 0.34 \text{ milligram,}$$

$$\frac{1000 \times 3}{5 \times 10^9 \times 365 \times 24 \times 60} \text{ of a gram of radium A, or } 0.0000000011 \text{ milligram and}$$

$$\frac{1000 \times 16}{5 \times 10^9} \text{ of a gram of radium D, or } 0.0032 \text{ milligram,}$$

all being calculated as elements.

Summary.—(1) The activity shown by radio-active substances is due to the spontaneous disintegration of the atom.

(2) A definite fraction of the total number of atoms present becomes unstable (it is not known why) in a given interval of time.

(3) The instability of the atom is shown by the emission of energy in the form of one α - or one β -particle, the latter usually being accompanied by γ -rays.

(4) The atom remaining after the expulsion of either particle is completely altered in chemical character. After the expulsion of an α -particle its atomic weight is four units less than that of its parent; after the expulsion of a β -particle parent and product have the same atomic weight.

(5) At any time there exists together :

(a) the unchanged radio-element.

(b) the product of disintegration.

(c) the product of (b), that product's product, and so on, if (b), (c) and products be radio-active.

(6) From (2) the period of average life and the half-value period of a radio-element may be deduced.

(7) At equilibrium the amounts of a parent substance and its successive products present together are directly proportional to their half-value periods.

CHAPTER IV

ATOMIC NUMBER, THE PERIODIC SYSTEM, AND THE STRUCTURE OF THE ATOM

UNTIL the year 1913 the Periodic System of Classification of the chemical elements was essentially that put forward by Mendeleef and Lothar Meyer in 1869-71. The classification was based on the idea that the properties of the chemical elements are a periodic function of their atomic weights. The atomic weight was considered to be an element's fundamental property, that on which in some way the others depended. The periodic classification was found to be a valuable one and was soon adopted by chemists, and will never, in all probability, be discarded. It systematised the whole subject of inorganic chemistry, and achieved striking success in many ways, particularly in showing at the time that certain elements were missing and predicting what the properties of these would be when they were found, predictions which were borne out very accurately, as is well known, when scandium, gallium, and germanium were discovered.

Nevertheless, certain difficulties were associated with it. The chief of these were :

- (a) The ambiguous position of hydrogen.

(b) The so-called exceptions in atomic weight :

(1) Argon 39·88 coming before potassium 39·10.

(2) Cobalt 58·97 before nickel 58·68.

(3) Tellurium 127·5 before iodine 126·92.

(c) The indefiniteness about the positions of the group of rare earths ; and the inability to predict their number whether missing or found ; hence inability to set a limit to the total number of elements in existence.

It was found, however, in 1913 by Moseley that the properties of the chemical elements are periodic functions not of their atomic weights, but of a more fundamental constant, the atomic number. The idea of atomic number has become of great importance in chemistry. It has carried one stage further the simplification which the periodic classification in its original form had made ; it has helped to shed much new light on the structure of the atom ; also it has removed the difficulties mentioned in the last paragraph. From work on atomic number it has been deduced :

(1) That hydrogen is not included in the periodic system.

(2) That argon does come before potassium, cobalt before nickel, and tellurium before iodine in the periodic classification.

(3) That the group of rare earths is not included in the periodic system.

(4) That the total number of elements in existence between hydrogen (of lowest atomic weight) and uranium (of highest atomic weight), is 92, and it indicates clearly the positions in the system of the five elements that are yet to be discovered.

Atomic numbers are determined experimentally. It is well known that an element may in suitable circumstances be caused to emit a characteristic X-radiation. There are three principal series of characteristic X-radiations known as the K-series, the L-series, and the M-series, the K being less penetrating (softer) than the L and the L than the M. X-radiations of the K-series are emitted by the elements from sodium to cadmium; of the L-series from zinc to uranium; and of the M-series from dysprosium to uranium. For any particular series the relation between the frequency n of the principal spectrum-line emitted by an element, and N the atomic number of the element, has been shown by Moseley and later workers to be connected by the simple relation

$$n = k N^2$$

where k is a constant for one series, but has different values for the three series.

Consider now the K-series, *i.e.* the characteristic X-radiations emitted by the elements from sodium to cadmium. If N for sodium be chosen as 11 (since it is the eleventh element in ascending order of atomic weights), the values of N for the other elements may be calculated from the experimental data. It is found that N for zinc is 30 and for cadmium 48.

Consider next the L-series, *i.e.* the characteristic X-radiation of the elements from zinc to uranium. N for zinc is already known, and from this value the values of N for the elements up to uranium can be determined. And so from the M-series.

In Fig. 4 the relation between n and N is shown

graphically. Obviously, since $n = k N^2$, N must be proportional to the square root of n , or to the reciprocal of the square root of λ the wave-length of the characteristic X-ray. Along the axis of Y are plotted values of $\sqrt{\frac{1}{\lambda}} \times 10^{-4}$, and along the axis of X the atomic numbers and the relation between them is a straight line.

In Table 5 the atomic numbers of the elements are shown in an up-to-date diagram of the periodic classification. (The elements enclosed by the thick black lines are radio-active.)

It may be seen from the figure or the table above that the atomic number is that obtained by numbering off the elements from hydrogen to uranium in ascending order of atomic weights with the following provisos :

(a) That argon comes before potassium, cobalt before nickel, and tellurium before iodine as the periodic classification has always indicated.

(b) That there is a space (corresponding to a missing element) between molybdenum and ruthenium, neodymium and samarium, tungsten and osmium, lead and emanation, and emanation and radium.

It is seen that the atomic number increases by one as we pass from any element to the one of next higher atomic weight (with the provisos mentioned). It is seen also that when the elements are arranged in order of atomic number, A and K, Co and Ni, Te and I are no longer exceptional, but in the places to be expected from their chemical properties. These facts show that atomic number is a more fundamental property of an element than atomic weight.

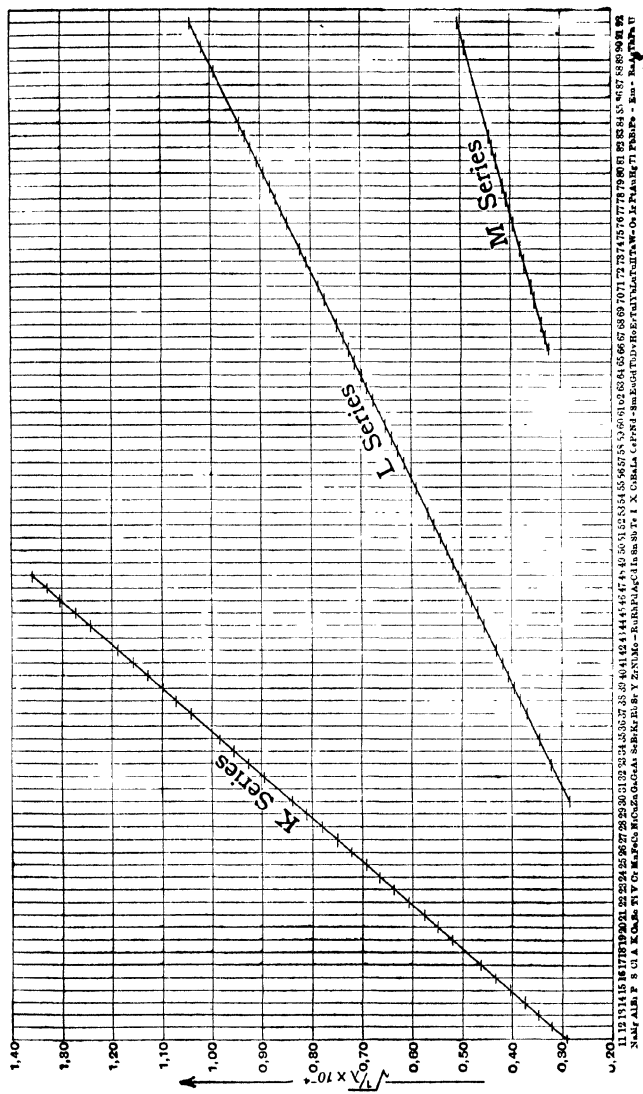


Fig. 4.

ATOMIC NUMBER AND FREQUENCY OF CHARACTERISTIC X-RADIATION (From Fajan's *Radioaktivitet*)

11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 46 87 88 89 90 91 92
Na Mg Al Si P S Cl Ar K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr Xe Rb Sr Y Zr Nb Mo Ru Rh Pd Ag Cd In Sn Sb Te I X Os La Ce Pr Nd Pm Sm Eu Gd Ho Er Tm Yb Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn - Ra - Ac - Th - Pa - U - Np - Pu - Am - Cm - Bk - Cf - Es - Fm - Md - No - Lr - La - Ce - Pr - Nd - Pm - Sm - Eu - Gd - Ho - Er - Tm - Yb - Lu - Hf - Ta - W - Re - Os - Ir - Pt - Au - Hg - Tl - Pb - Bi - Po - At - Rn - Ra - Ac - Th - Pa - U - Np - Pu - Am - Cm - Bk - Cf - Es - Fm - Md - No - Lr

As each element has but one atomic number, and the highest atomic number known is 92, there cannot be more elements between hydrogen and uranium inclusive than 92. Eighty-seven of these, as the diagram shows, have been discovered, and the positions of the five still to be discovered, numbers 43, 61, 75, 85, and 87, are definitely known.

Rydberg's formula.—An ingenious formula has been suggested for calculating the atomic numbers of the elements of group O. It is :

$$N_{\text{Group O}} = 2\Sigma(1 + 2^1 + 2^2 + 3^1 + 3^2 + 4^1 + \dots) \quad (1)$$

where $N_{\text{Group O}}$ represents the atomic number of an inert element.

From (1) :

$$N_{\text{He}} = 2 \times 1 = 2$$

$$N_{\text{Ne}} = 2(1 + 2^1) = 10$$

$$N_{\text{Ar}} = 2(1 + 2^1 + 2^2) = 18$$

$$N_{\text{Kr}} = 2(1 + 2^1 + 2^2 + 3^1) = 36$$

$$N_{\text{Xe}} = 2(1 + 2^1 + 2^2 + 3^1 + 3^2) = 54$$

$$N_{\text{Em}} = 2(1 + 2^1 + 2^2 + 3^1 + 3^2 + 4^1) = 86$$

If the positions and names of the elements in the neighbourhood of an inert element be known, their atomic numbers are easily calculated by the help of the above formula. To calculate that of barium, remember it is in Group II and near xenon. Xenon's atomic number is $2(1 + 2^1 + 2^2 + 3^1 + 3^2)$, i.e. 54; and as xenon is in Group O and barium in Group II, the latter's atomic number is 56.

By careful use of this formula and knowledge of the members of the different groups of the periodic system, the atomic numbers of all the elements may quickly

be written down. It is likely that atomic number and not atomic weight will figure in the textbooks of the future as the fundamental constant of a chemical element.

The constituents of the atom.—The atoms of all the chemical elements are believed to be built up in the same general way. The present view of the atom is that it is made up of positive and of negative electricity. On Rutherford's theory, at the atom's centre is a nucleus of positive electricity which is very small compared with the dimensions of the atom. (An atom has a radius of about 10^{-8} cm., the nucleus about 10^{-15} cm.). This contains, nevertheless, almost the whole of the atom's mass, and carries a charge of positive electricity equal to some multiple of the unit charge of electricity, namely, that of an electron. The nucleus may, and in the atoms of heavy atomic weights the nucleus does, contain both positive and negative charges, but since the former is always greatly in excess of the latter, the net charge is positive.

Round the nucleus are disposed charges of negative electricity (electrons) equal in number to the net positive charge on the nucleus. Their disposition is not fully known at present, and need not concern us here. The essential points are that each electron is one single negative charge of electricity, that its mass is an insignificant part of the atom's mass (being about $\frac{1}{1836}$ of the mass of a hydrogen atom), and its volume a very small fraction of that of the atom. (If it be assumed spherical, the radius of it is about 10^{-13} cm. Note that it is larger than the nucleus.)

To contrast negative and positive electricity in the

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atom. The electrons external to the nucleus are discrete single charges of electricity. They are not associated. The expulsion of one from an atom causes the resultant atom to have a positive charge, but has an almost negligible effect on the atom's mass. Positive electricity in the nucleus consists of many positive (and in some atoms negative) charges associated. The loss of one positive charge causes the resultant atom to have a negative charge, and also a smaller atomic mass, for experiment shows that for each positive charge expelled by the atom, two units of atomic weight are lost.

Since the atom is assumed to be normally neutral, the (net) number of positive charges on the nucleus and the number of external electrons are equal. This number has been shown experimentally to be the atomic number. Thus the hydrogen atom (atomic number 1) consists of a single positive charge on the nucleus and a single external electron; the helium atom (atomic number 2) of two positive charges on the nucleus and two external electrons, and so for atoms of all the elements. The atomic number is the number of external electrons; also the net number of positive charges on the nucleus.

The charge on the nucleus determines the configuration of the external electrons, and since the configuration of the external electrons is assumed to be the seat of all ordinary physical and chemical properties of the atom, the charge on the nucleus is the fundamental property of the atom. On it the physical and chemical properties depend. If it be altered in any way so that the charge is decreased or increased, the

TABLE 5.—THE PERIODIC SYSTEM TO-DAY

0	Group VIII	I		II		III		IV		V		VI		VII	
		a	b	a	b	a	b	a	b	a	b	a	b	a	b
2 He		3 Li		4 Be		5 B		6 C		7 N		8 O		9 F	
10 Ne		11 Na		12 Mg		13 Al		14 Si		15 P		16 S		17 Cl	
18 A		19 K		20 Ca		21 Sc		22 Ti		23 V		24 Cr		25 Mn	
26 Fe 27 Co 28 Ni		29 Cu		30 Zn		31 Ga		32 Ge		33 As		34 Se		35 Br	
36 Kr		37 Rb		38 Sr		39 Y		40 Zr		41 Nb		42 Mo		43 —	
44 Ru 45 Rh 46 Pd		47 Ag		48 Cd		49 In		50 Sn		51 Sb		52 Te		53 I	
54 Xe		55 Cs		56 Ba		57 La, 58 Ce, 59 Pr, 60 Nd, 61 —, 62 Sm, 63 Eu, 64 Gd, 65 Tb, 66 Dy, 67 Ho, 68 Er, 69 Tm, 70 Yb, 71 Lu, 72 Hf, 73 Ta, 74 W, 75 —									
76 Os 77 Ir 78 Pt		79 Au		80 Hg		81 Tl		82 Pb		83 Bi		84 Po		85 —	
86 Em		87 —		88 Ra		89 Ac		90 Th		91 Pa		92 U		93 —	

configuration of the external electrons will be radically altered, and the physical and chemical properties likewise will be radically altered ; alteration of the charge on the nucleus, therefore, leads to an entirely different atom.

Three facts may be emphasised in connection with this.

(1) The chemical elements are apparently not so independent of one another as chemists thought prior to the discovery of radio-activity. It has been found, as has been said above, that all have essentially the same structure. The difference between one element and another is largely a difference in the amount of charge carried by the nuclei of the two sets of atoms.

(2) The nature and magnitude of the nucleus of the atom has been shown by recent work in physics to be such that an alteration of the nucleus by artificial means is an extraordinarily difficult undertaking. Change of such conditions as temperature or pressure has no effect on the nucleus. This difficulty in attacking the nucleus explains why it is that, although the difference between the atoms of different elements is a simple one, it is very difficult to bring about transmutation of one element into another artificially.

(3) Radio-elements are those whose atoms' nuclei are *spontaneously* and continuously being transformed into the nuclei of atoms of other elements.

CHAPTER V

THE THREE DISINTEGRATION SERIES

IN Chapter III it was mentioned that there are three disintegration series, those of uranium, actinium, and thorium. A short account will now be given of the experiments which led to the elucidation of these series; and the chief facts relating to the chemistry of the different members of the series will be summarised for reference in three tables. The facts of importance are:

(a) The element to which the radio-element of the series has experimentally been proved to be chemically most similar. This is a convenient way of expressing chemical properties in a short form.

(b) The position of the element in the disintegration series.

(c) The atomic weight of the radio-element. This is most frequently calculated from reliable data. In a few cases it has been determined directly.

(d) The radiation expelled by the radio-element. This would appear to be of physical interest only. It will be shown later, however, that the nature of the radiation expelled by a body fixes the chemical properties of its product.

(e) The half-value periods.

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(a) will be discussed in Chapter VI; (b) and (c) will be separately considered below for each of the three series; (d) and (e), which apply generally, will be considered first.

The radiations and their detection.—Radio-active radiations are usually detected and measured in three ways:

- (1) By their ionisation effect in air or other gas.
- (2) By their effect on a photographic plate.
- (3) By their effect on a fluorescent screen.

For details of these methods *Rutherford* should be consulted.

The α -particle.— α -particles are easily distinguished from β -particles and γ -rays by their—

(a) Absorbability. They are the most easily absorbed of the three types. 10 cm. of air or $\frac{1}{16}$ mm. of aluminium stops them completely.

(b) Behaviour in an electric or a magnetic field, since they are positively charged.

On account of their great energy, they produce very intense ionisation in the gas through which they pass. Weak preparations expelling α -particles are therefore most conveniently measured by the rate of discharge of the leaf of a gold-leaf electroscope.

The action of α -particles on a photographic plate is very weak.

They produce fluorescence on a prepared screen such as one of crystals of zinc sulphide. If this fluorescence be observed through a low-power microscope, it is found to consist of a succession of scintillations produced by the successive impacts of individual α -particles. Each particle produces a separate flash

on the screen when it strikes it. The impact of a single α -particle can thus be observed. One α -particle alone is expelled per atom when an element expelling α -particles disintegrates.

The β -particle.— β -particles are easily distinguished from the two other types by their—

(a) Absorbability. They may penetrate up to 3 mm. of aluminium and corresponding thicknesses of other materials.

(b) Behaviour in an electric or a magnetic field, since they are negatively charged. They are many times more easily deviated (and of course in the opposite direction) than α -particles.

They have a marked effect on a photographic plate.

Their ionising—and fluorescent—effect is many times less than that of the α -particle. A single β -particle has not yet been detected by the fluorescent screen. They are usually detected and measured by their ionisation effect in a gold-leaf electroscope, the active preparation being covered to prevent any ionisation effect due to α -particles which may be simultaneously expelled.

One β -particle alone is expelled per atom when a radio-element expelling β -particles disintegrates.

The γ -ray.— γ -rays carry no electric charge, and are the most penetrating of the three types. For example, the γ -rays from radium C can be detected after they have passed through 30 cm. of iron. They are not deflected in the least degree either by an electric or a magnetic field.

They have a relatively feeble effect in ionising gases, affecting a photographic plate or producing luminosity

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on a prepared screen. Typical electroscopes used in working with α -, β -, and γ -ray bodies are shown in Fig. 5.

In considering radio-activity from the chemical side, the γ -ray has not the importance of the other two types, which are a primary disturbance of the nucleus and cannot be expelled from an atom without a fundamental change taking place. The γ -ray is a secondary

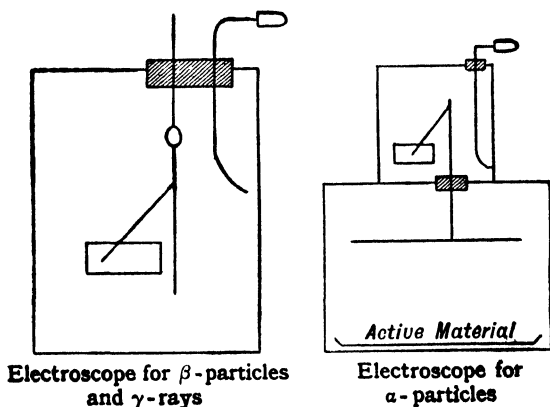


FIG. 5.

disturbance, an effect due in all probability, in the main, to the sudden emission of a β -particle from the nucleus. Its expulsion from an atom does not of itself cause a new atom to be produced. γ -rays are usually measured by their ionisation effect in a gold-leaf electroscope whose walls and base are thick enough to exclude β -particles.

Half-value periods.—The half-value periods of the radio-elements set out in the tables in this chapter

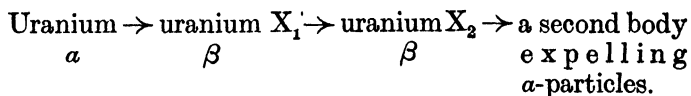
have been determined for the most part directly, *i.e.* by separating the particular radio-element chemically, and measuring from time to time the ionisation effect of its rays in an electroscope ; or by determining the weights of the equilibrium-amounts of parent and product and assuming the period of one of them ; or by measuring on a fluorescent screen the number of α -particles expelled by a known mass of an element in a given time. (For knowing the mass of the element one can calculate the number of atoms in it, and knowing the number of these which are transformed in a given time, one can calculate the rate of transformation, and therefore the half-value period.)

The half-value periods of the quickly-changing elements have been determined by special methods, or, failing a direct experimental method, have been calculated from their physical properties.

THE URANIUM SERIES

Radio-activity was discovered in a compound of uranium by Becquerel, and later but independently by Silvanus Thompson in 1896. We know now that what Becquerel first discovered was really the radio-activity not of uranium itself, but of its product uranium X. A compound of uranium shows both α - and β -particle activity, the former from uranium, the latter from its product, which is normally in equilibrium with it. Crookes in 1900 showed that the radio-activity of uranium, in so far as it affected a photographic plate (that due to the β -particles), could be removed as a minute precipitate by chemical means

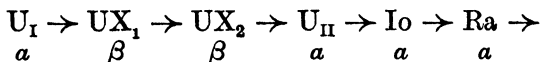
from the uranium compound, and this body he called uranium X because of its new and mysterious character. Later, because of an analogy with other β -particle products, it was suspected that uranium X consisted of two successive β -particle products, and on this being proved experimentally by Fajans and Roth in 1913, the two bodies were called uranium X_1 and uranium X_2 . Boltwood in 1906, from physical measurements on the α -particle activities of uranium and its products in an old mineral, concluded that uranium itself expelled approximately twice as many particles as the simple theory suggested. It was thought at first that uranium expelled in succession two α -particles, but later it was concluded that there were two bodies and not one expelling α -particles, the second of these being the product of uranium X_2 . The series thus runs :



This last body and uranium have been found to possess identical chemical properties, consequently if the two be mixed, as they are in minerals, separation is impossible. What is called the element uranium is on this view really a mixture of two elements which differ in atomic weight by four units, and in radioactive properties, but are identical in other properties. The first of these is called uranium I, and the second uranium II. The proportion in which these two make up uranium is calculable, as has been mentioned when discussing the disintegration theory, being the ratio of their half-value periods, which is approxi-

mately 5,000 to 1. From this it follows that the mean atomic weight of the mixture is approximately that of uranium I. All compounds of uranium in existence are mixtures of compounds of these two elements.

Radium was discovered in 1898 by M. and Mme Curie in pitchblende. The name was suggested by the rays it spontaneously emitted. Its connection with and place in the uranium disintegration series was discovered some years later by the researches of Soddy and of Boltwood. The former showed that in a carefully purified preparation of uranium, radium very gradually was produced, and his experiments proved not only the genetic connection of radium and uranium, but also that at least one new element of long half-value period lay between. Boltwood showed that in *all* old untouched minerals containing uranium the ratio of the weights of radium to uranium was constant. This proves genetic connection as has been discussed in p. 29 above. In 1907 Boltwood isolated a new radio-element called ionium (after the word *ion*), which he showed was the parent of radium. This body has a long half-value period and is the body suggested by Soddy's experiments. In 1913, as a result of a survey of both the physical and chemical evidence, ionium was found to be the product of uranium II. The series consequently runs:



The disintegration product of radium is gaseous, a homologue of the group of inert gases of the periodic

classification, and is called the radium-emanation. Except in its radio-activity, its behaviour is that to be expected from its position in that group.

The radio-elements which follow the radium-emanation in the disintegration series consist of three bodies of relatively short half-value periods and three of relatively long. The first three are often referred to as "the active deposit of short life," or more briefly as "the active deposit," and the last three as "the active deposit of long life." The reasons for these names are that RaA, RaB, and RaC have relatively short periods, RaD, RaE, and RaF relatively long periods, and all are solids which are consequently deposited on any material which has been exposed to the gaseous disintegrating emanation.

The deposit is easily removed by hot acids from the walls of the glass tube (or from a wire inserted in the tube) on which it is formed, and may be analysed partly by physical measurements—namely, by the rate of decay and growth of the material in different circumstances—and partly by the chemical methods used in radio-activity—namely, chemical operations controlled at every stage by measurements of α - and β -particles in an electroscope.

These analyses reveal the presence of six successive products which have been named systematically radium A, radium B to radium F. From radium, therefore, the series runs:

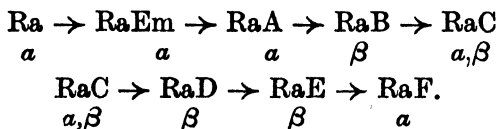


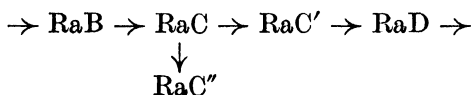
TABLE 6.—THE URANIUM SERIES.

<i>Element.</i>	<i>Symbol.</i>	<i>Radiation.</i>	<i>At. Wt.</i>	<i>Half-value Period.</i>	<i>Element chemically Similar.</i>
Uranium I . . .	U _I	α	238·2	$4·7 \times 10^9$ Y	U
Uranium X ₁ . . .	UX ₁	β, γ	234	24·6 D	Th
Uranium Z . . .	UZ	β, γ	(234)	6·8 H	Pa
Uranium X ₂ . . .	UX ₂	β, γ	234	1·15 M	Pa
Uranium II . . .	U _{II}	α	234	About 2×10^6 Y	U
Uranium Y . . .	UY	β, γ	(230)	25 H	Th
Ionium . . .	Io	α	230	About 10^6 Y	Th
Radium . . .	Ra	α, β	226	1,600 Y	Ra
Radium-emanation	RaEm	α	222	3·85 D	Em
Radium A . . .	RaA	α	218	3·0 M	Po
Radium B . . .	RaB	β, γ	214	26·8 M	Pb
Radium C . . .	RaC	(α), β, γ	214	19·5 M	Bi
Radium C' . . .	RaC'	α	214	About 10^{-6} S	Po
Radium C'' . . .	RaC''	β	210	1·4 M	Tl
Radium D . . .	RaD	β, γ	210	16 Y	Pb
Radium E . . .	RaE	β, γ	210	5·0 D	Bi
Radium F . . . (Polonium)	RaF or Po	α	210	136 D	Po
Radium G . . . (Uranium Lead)	RaG or Pb _U	Inactive	206	—	Pb

(Y = years, D = days, M = minutes, S = seconds)

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Radium A, radium B, radium C, and radium E were discovered by physical and chemical analyses of the active deposit. Radium C was subsequently shown to break up in two ways, a large fraction of atoms forming a new body called radium C', which on disintegration formed radium D, and a small fraction forming a new body called radium C". This branching will be discussed later. The series therefore should run :



Radium D is the same body as radio-lead, discovered, as has been mentioned, in uranium minerals in 1901, and then so named from its chemical character. Radium F is the same as polonium, discovered in 1898 by Mme Curie and named after Poland, her native country.

The transformation product of polonium, radium G, is often called "the end-product" because, being inactive, the uranium series stops with it. As it is chemically identical with ordinary lead, however, it is often referred to as "uranium-lead," which describes it characteristically.

In Table 6 is set out the uranium disintegration series as it is at present known, with the particulars mentioned under the headings (a), (b), (c), (d), and (e) above as up-to-date as possible.

Atomic weights of members of the uranium series.—In Table 6 above, the atomic weights shown in

heavy type have been determined experimentally. They are all recent redeterminations by Hönigschmid and his co-workers. To the second decimal place the values are $U = 238.20$, $Ra = 225.97$, and $Pb_U = 206.05$. Since the α -particle weighs 4.00 and the β -particle is of negligible weight, it is possible to calculate the atomic weights of all the elements of this series. The difficulty is to decide which of the three experimental values to select as datum. If Ra be taken as 226.0, Pb_U should be 206.00 and U should be 238.0 by allowing for the α -particles expelled. The difference between the calculated and the experimental value of Pb_U , taking $Ra = 226$ as datum, is not important, but a satisfactory account of the discrepancy between the corresponding values of U has not yet been given. In the table the calculated atomic weights are based on $Ra = 226.0$, and the α -particle = 4.00. The atomic weights of UZ and UY given in brackets are calculated on the assumption that these bodies occupy the positions assigned to them in the table.

Branching in the uranium series.—In Table 6 each element is the product of the one next above it, or as indicated by the arrows. Usually a radio-element is wholly transformed into its product. A few, however, appear to break up in two different ways, the larger fraction of atoms breaking up into one product termed the main product, and the smaller into a second product called the branch product. 99.97% of RaC breaks up with the expulsion of a β -particle to form RaC', 0.03% breaks up with the expulsion of an α -particle to form RaC". U_{II} is believed to give two products also. 96.7% of U_{II} breaks up with the expulsion of an α -

particle to form Io, 3.3% breaks up with the expulsion probably of an α -particle to form UY. Io is the main product, and its successive products form the main uranium series; UY is the branch product, and its successive products form a branch series which is believed to be the actinium series.

UX₁ expels a β -particle and gives UX₂; it also expels a β -particle and gives UZ. The fractions breaking up to form these products are not yet known. Both UX₂ and UZ are chemically similar, and both appear to disintegrate to form U_{II}. They are known to be different bodies only because they have different half-value periods.

Nomenclature.—Although the elucidation of the three series of radio-elements is now nearly complete, a systematic nomenclature has not yet been adopted. For the most part the elements were named by their discoverers, and as they were not discovered in the order in which they stand in Table 6, the nomenclature is haphazard. In recent years certain small changes have been adopted to show more clearly the similarities of the three series, and to make the names as systematic as possible without introducing radical changes.

If a body has subsequently been shown to consist of two isotopes, these are indicated by Roman indices, thus: U_I, U_{II}; and by Arabic indices if the body has been subsequently shown to consist of two successive products, thus: UX₁, UX₂. For the branch products of the C-members, one dash indicates the isotopes of polonium, two dashes the isotopes of thallium. Thus RaC', AcC', and ThC' are isotopic

with polonium, and RaC'' , AcC'' , and ThC'' with thallium. The original name UY, however, is retained for the branch product of U_{II} at the head of the actinium series, and UZ has been given to the new element believed to be a branch product of UX_1 .

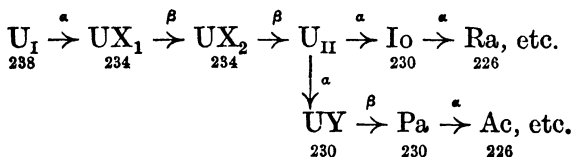
THE ACTINIUM SERIES

The actinium series derives its name from actinium, the second member of the series but the first to be discovered. It was discovered by Debierne in 1899, and was later believed to be an element of long half-value period and to be the head of the series. Subsequent experimental work showed, however, that its period was twenty years only. A search was then made for its parent substance. This was discovered in 1917 independently by Hahn and by Soddy in pitchblende residues.

Protactinium, although considered to be a primary radio-element, because it is the head of the actinium series, is probably genetically connected with uranium. Boltwood showed that in old minerals there is a constancy of proportion between the amounts of uranium and actinium in different minerals, showing that actinium is genetically connected with uranium. (The argument holds equally well for protactinium, which was not discovered at this time.) The amount of actinium found, however, is much less than to be expected if it were a direct product of disintegration. Presumably it lies, therefore, in a side-chain. At the present moment it is not known precisely how protactinium arises from uranium, but three schemes have

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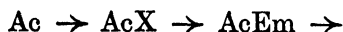
been suggested. All these consider that protactinium is the product of uranium Y. The first states that uranium Y is the product of uranium I, the second that it is the product of uranium II, and the third that it is the product of an isotope of uranium which may or may not be connected with uranium I and II. The first of these views is considered unlikely. The writer inclines to the third, but as the second is considered at present the most probable it is given here, *viz.* :



The third scheme is given alternatively with the above in Fig. 6 (p. 59).

The second part of the actinium series (from actinium onwards) is much better known. It has been elucidated experimentally.

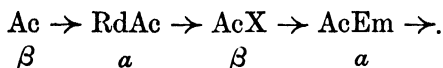
Preparations of actinium, like those of radium, produce a gaseous emanation which is itself radioactive. It was found that the parent of this emanation was easily removed chemically from actinium as a minute precipitate. Because of this it was called actinium X by analogy with uranium X, and the series was believed to run :



actinium expelling both α - and β -particles.

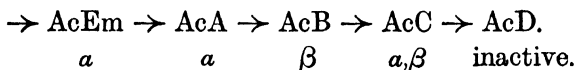
Hahn showed, however, that a product existed between actinium and actinium X, which he called radio-actinium, because it expelled the whole of the α -particles ascribed to actinium. Actinium itself emits a feeble β -radiation only.

The series therefore runs :

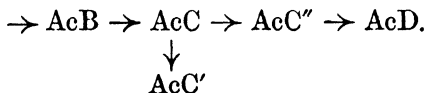


Like the radium emanation, the actinium emanation produces an active deposit on all bodies exposed to it. Careful analysis of this reveals the presence of four successive transformation products named by analogy with the first four of the radium active deposit: actinium A, actinium B, actinium C, and actinium D. The last of these, being inactive, is the end-product of the series.

This part of the series runs :



Subsequently AcC, like RaC, was found to break up in two ways, the larger fraction breaking up into AcC'', which on disintegration produces AcD, and the smaller fraction into AcC'. This is discussed later. The series therefore should run :



In Table 7 is set out the particulars of the actinium

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disintegration series, corresponding to those for the uranium series in Table 6.

Atomic weights of members of the actinium series.—The atomic weights of the members of the actinium

TABLE 7.—THE ACTINIUM SERIES

<i>Element.</i>	<i>Symbol.</i>	<i>Radiation.</i>	<i>At. Wt.</i>	<i>Half-value Period.</i>	<i>Element chemically Similar.</i>
Protactinium	Pa	α	(230)	12,000 Y	Pa
	↓				
Actinium	Ac	β	(226)	About 20 Y	Ac
	↓				
Radio-actinium	RdAc	α, β, γ	(226)	19 D	Th
	↓				
Actinium X	AcX	α, β	(222)	11.5 D	Ra
	↓				
Actinium-emanation	AcEm	α	(218)	2.92 S	Em
	↓				
Actinium A	AcA	α	(214)	0.002 S	Po
	↓				
Actinium B	AcB	β, γ	(210)	36.1 M	Pb
	↓				
Actinium C	AcC	$\alpha(\beta)$	(210)	2.15 M	Bi
	↓ ↘				
Actinium C'	AcC'	α	(210)	0.005 S	Po
	↓ ↙				
Actinium C''	AcC''	β, γ	(206)	4.71 M	Tl
	↓ ↘				
Actinium D (Actinium Lead)	AcD	Inactive	(206)	—	Pb

(Y = years, D = days, H = hours, M = minutes, S = seconds.)

series are calculated on $UY = 230$, UY being the parent of Pa, and the α -particle = 4.00. The view adopted of the relation of UY to the uranium series is that set out above, namely, that it is the branch-product of U_{II} .

If $UY = 230$, $Pa = 230$, and the atomic weights of the other products are calculated from the latter. If the parent of Pa should be the branch-product of U_I , all the atomic weights given in Table 6 must obviously be increased by 4.

Branching in the actinium series.—Corresponding to RaC , AcC breaks up in two ways. 99.85% of it breaks up with the expulsion of an α -particle to form AcC'' , 0.15% with the expulsion of a β -particle to form AcC' .

THE THORIUM SERIES

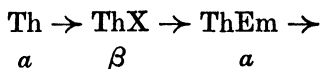
Thorium was the second radio-element to be discovered (Mme Curie and G. C. Schmidt, 1898), and will always be interesting historically, for it was experimental work on preparations of thorium that led Rutherford and Soddy to the disintegration theory.

Preparations of thorium compounds, like those of uranium, expel both α - and β -particles, but in addition they produce a gaseous radio-active element, the emanation. Rutherford and Soddy showed that in thorium preparations two solid radio-active substances were present, and that the body expelling β -particles could be completely separated by chemical means from that expelling α -particles. They showed, further, that the β -particle body was the one which generated the emanation. It was exceedingly minute in amount, for after its removal from the thorium compound there was no measurable diminution of the latter. This β -particle product was called, by analogy with uranium X,

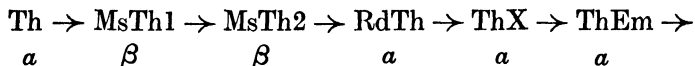
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thorium X, and thorium itself was believed to be directly transformed into thorium X.

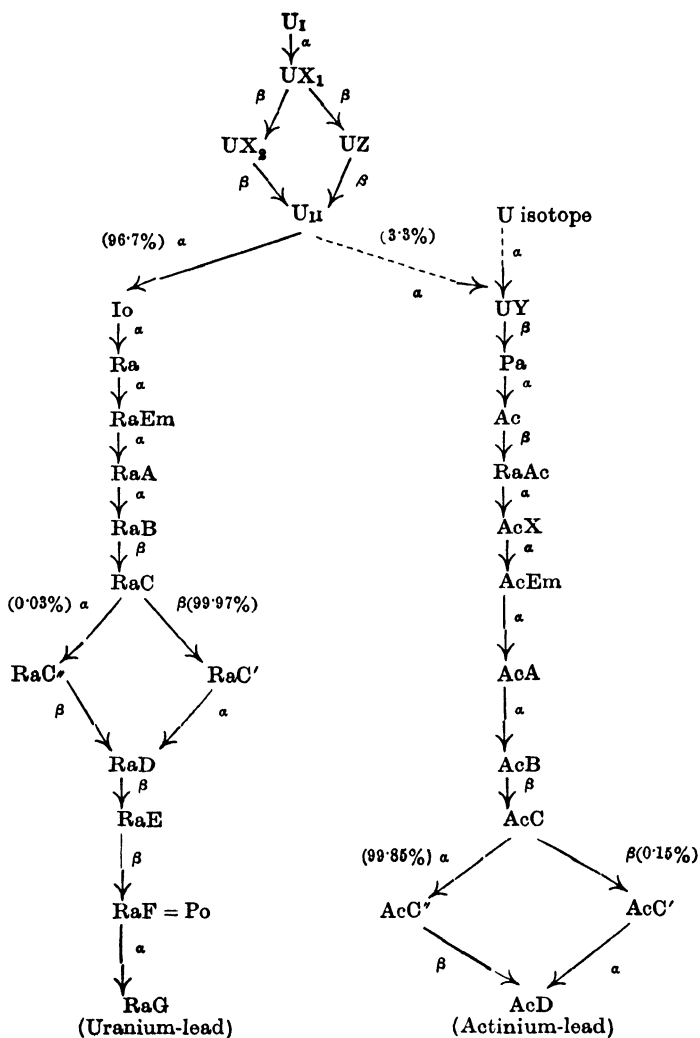
The series consequently was believed to run :



Later work showed that the series was more complex. Hahn showed, from an extensive study of thorium minerals and thorium preparations of different ages, that no less than three radio-active bodies existed between thorium and thorium X. A body expelling α -particles he called radio-thorium, and this was proved to be the true parent of thorium X. Between thorium and it a body expelling β -particles was found, and this he called mesothorium. Later he proved this body to be complex; it consists of two products each expelling β -particles. They were named mesothorium 1 and mesothorium 2. The first part of the thorium series therefore runs :



The active deposit of thorium emanation has been analysed in the same way as those of radium and actinium emanations. It consists of four successive products—thorium A, thorium B, thorium C, and thorium D. These resemble very closely the corresponding products in the radium and actinium series. Thorium D, like actinium D, but unlike radium D, is



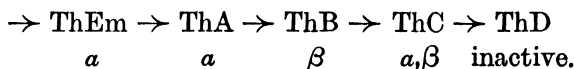
The dotted lines between U_{II} and UY and U isotope and UY indicate alternative possibilities.

FIG. 6.—THE URANIUM DISINTEGRATION SERIES.

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the end-product, and consequently the series stops with it.

The latter part of the series runs :



Subsequently ThC, like RaC and AcC, was found to

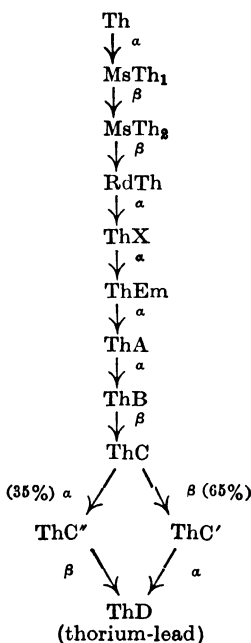
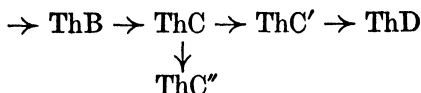


FIG. 7.—THE THORIUM DISINTEGRATION SERIES.

break up in two ways, the larger fraction breaking up into ThC', which on disintegration produced ThD, and the small fraction breaking up into ThC''.

This is discussed later. The series therefore should run :



In Table 8 is set out the particulars of the thorium:

TABLE 8.—THE THORIUM SERIES

<i>Element.</i>	<i>Symbol.</i>	<i>Radiation.</i>	<i>At. Wt.</i>	<i>Half-value Period.</i>	<i>Element chemically Similar.</i>
Thorium . .	Th	α	232·15	About $1\cdot5 \times 10^{10}$ Y	Th
	↓				
Mesothorium 1 .	MsTh ₁	β	228	6·7 Y	Ra
	↓				
Mesothorium 2 .	MsTh ₂	β, γ	228	6·2 H	Ac
	↓				
Radiothorium .	RdTh	α, β, γ	228	1·9 Y	Th
	↓				
Thorium X . .	ThX	α	224	3·64 D	Ra
	↓				
Thorium-emanation	ThEm	α	220	54·5 S	Em
	↓				
Thorium A . .	ThA	α	216	0·14 S	Po
	↓				
Thorium B . .	ThB	β, γ	212	10·6 H	Pb
	↓				
Thorium C . .	ThC	$(\alpha)\beta$	212	60·8 M	Bi
	↓				
Thorium C' . .	ThC'	α	212	About 10^{-11} S	Po
	↓				
Thorium C'' . .	ThC''	β, γ	208	3·1 M	Tl
	↓				
Thorium D . .	ThD	Inactive	208	—	Pb
(Thorium Lead)					

(Y = years, D = days, H = hours, M = minutes, S = seconds.)

The atomic weights shown in heavy type have been determined experimentally. The others have been calculated from that of ThD.

disintegration series corresponding to the particulars given in Tables 6 and 7.

Branching in the thorium series.—ThC, like RaC and AcC, breaks up in two ways: 65% of it breaks up with the expulsion of a β -particle to form ThC', 35% with the expulsion of an α -particle to form ThC''.

Below are set forth, in Figs. 6 and 7, the uranium and thorium disintegration series to show the branchings that occur, and to make plain the supposed genetic relationship of the actinium to the uranium series. These diagrams embrace the data given above and supplement Tables 6, 7, and 8.

CHAPTER VI

THE TEN TYPES OF RADIO-ELEMENTS AND THE GROUP-DISPLACEMENT LAW

IN the last columns of the three tables in the preceding chapter are given the elements to which the radio-elements tabulated there have been found experimentally to be chemically most similar. This is a convenient way of expressing in brief their chemical characters and, as will be seen, an exact way. It may seem curious at first to chemists that an investigation of the chemical properties of new elements like the radio-elements should have received the little importance it did in the early days of radio-activity. It was not till 1913 that a systematic investigation of this subject was completed. Except in a few instances—that of radium, for example—the problem was not faced. The reason for this is that workers in radio-activity were so engrossed in investigating the radio-active properties of these new and interesting bodies that to them an investigation of their chemical properties seemed almost irrelevant.

It must also be remembered that the concentration of most of these bodies was so excessively small that many early workers were doubtful whether the bodies could be said to have chemical properties in the

ordinary sense at all. So long as sufficient of the radio-active body was separated chemically to enable its radio-active properties to be investigated, there was little stimulus to devise the best methods, *i.e.* to investigate the chemical properties of the substance. Many of the original methods of separation we now know to be poor ones; some, indeed, depended upon partial adsorption of the minute but highly active substance. It was shown, however, by Schrader in 1911 that the constituents of the active deposits formed chemical compounds, and behaved chemically in every way like ordinary elements, and gradually it was shown that all radio-elements behaved similarly.

It was next found that when the chemical properties of the radio-elements were investigated systematically, there was always a common element (by which is here meant one for which there is a place in the periodic classification) which resembled the radio-element chemically more than another. These are they given in the last columns of Tables 6, 7, and 8 above. The details of the methods employed are given later in Chapter XI, but the principle on which the investigation depended may be outlined briefly. To a solution containing one or more radio-elements a solution of the principal common elements was added. The common elements were then separated out in the usual way, and each of these was examined for radio-activity by the usual methods with electroscopes. It was found that each radio-element attached itself definitely to one particular element in all circumstances. This located approximately the common

element which the radio-element most closely resembled. Next the experiment was repeated with all the elements, which resembled this common element, mixed with the particular radio-element under investigation, and the particular one which, when separated from the others, carried with it the radio-element discovered.

For example, ionium is not precipitated as chloride along with lead, silver, or mercurous compounds, nor with any of the group which is precipitated by H_2S from a solution containing HCl . It is precipitated quantitatively, however, with iron, chromium, and aluminium by NH_4OH and NH_4Cl . This indicates ionium's analytical behaviour approximately. A second experiment is carried out with a solution of ionium mixed with a solution of compounds of all the elements which in the course of analysis are precipitated by NH_4OH and NH_4Cl . These are separated from one another by the usual methods, and each tested for radio-activity by the electroscope. It is found that ionium *invariably* cleaves to the thorium, eschewing all others; thorium is consequently regarded as the *common* element to which ionium is chemically most akin. And so for the others.

It is seen from Tables 6, 7, and 8, on pp. 49, 56, 61, that altogether there are but ten different elements which possess chemical properties most similar to the forty known radio-elements, a very remarkable result. These ten may be conveniently described as *types of radio-elements*. Their atomic numbers, names, and positions in the periodic system are given in the following table :

TABLE 9.—TYPES OF RADIO-ELEMENTS

<i>Column of Periodic Table.*</i>	<i>At. No.</i>	<i>Type.</i>	<i>Members of Group.</i>
VIA . . .	92	Uranium	— — Cr, Mo, W, U
VA . . .	91	Protactinium	— — V, Cb, Ta, Pa
IVA . . .	90	Thorium	C, Si, Ti, Zr, Ce(?) Th
IIIA . . .	89	Actinium	B, Al, Sc, Yt, La, Ac
IIA . . .	88	Radium	Be, Mg, Ca, Sr, Ba, Ra
0 . . .	86	Emanation	He, Ne, A, Kr, Xe, Em
VIB . . .	84	Polonium	O, S, Se, Te, Po
VB . . .	83	Bismuth	N, P, As, Sb, Bi
IVB . . .	82	Lead	C, Si, Ge, Sn, Pb
IIIB . . .	81	Thallium	— — Ga, In, Tl

* A = first octave, B = last octave, of a long period.

Note that there are no type elements corresponding to atomic numbers 87 and 85. These are still to be discovered. 87 is the homologue of the group of alkali metals, 85 that of the halogen group. Both, when discovered, will probably be radio-active.

Of the ten types, five were known before the discovery of radio-activity. The five discovered since are protactinium, actinium, radium, emanation, and polonium. Protactinium has been proved to be the homologue of tantalum, actinium of lanthanum and the rare earth group, radium of barium, the emanation of xenon and the inert gases of the helium group, and polonium of tellurium.

The whole of the radio-elements, then, have been found experimentally to be divided into ten groups, every member of a group being similar chemically to one of the ten types, more similar to it than to any other chemical element. The three disintegration series will now be set out diagrammatically, so that

while the relation between successive members of a disintegration-series is preserved, every radio-element is placed vertically above the type element to which it has been found chemically similar. This is done in Fig. 8 on p. 69.

The members of a group all of which are similar to a type element (the members of each vertical column) are usually referred to as isotopes, so named by Soddy, because they occupy the same place in the periodic classification (Greek, *ἴσος*, equal, *τόπος*, place).

This diagram is convenient because, in addition to setting out the three disintegration series, it shows the different sets of isotopes in their proper places in the periodic system, and it also demonstrates a very simple relation between the position of a radio-element in the periodic table and the radiation expelled by the element of which it is the product. This relation may be expressed thus :

(1) *When an element expels an α -particle (carrying two positive charges) its atomic number is diminished by 2, i.e. the product occupies a position in the periodic system two places lower than the parent element.*

(2) *When an element expels a β -particle (carrying one negative charge) its atomic number is increased by 1, i.e. the product occupies a position one place higher in the table than the parent element.*

These rules, known now as the Group-Displacement Law, were first put forward (but in an imperfect form) by the writer from imperfect chemical evidence, and before the three disintegration series were unravelled as completely as they are at present ; and more correctly later by Fajans and by Soddy (1913). They are now

thoroughly substantiated, as may be seen by comparing Fig. 8 with the data of Tables 6, 7, and 8.

The Group-Displacement Law was found out before the theory of atomic number was put forward. It is, however, an obvious deduction from that theory. For the atomic number, it has been mentioned, is identified with the net number of positive charges on the atom's nucleus. Clearly, if the nucleus gives up two of these, as it does when it expels an α -particle, the atomic number is diminished by two; a negative charge lost is the equivalent of a positive gained, so that when a β -particle is expelled the atomic number is increased by one.

It should be noted that the expulsion of the γ -ray has no such effect as that of an α - or β -particle.

Whenever it happens that an element expels *both* an α - and a β -particle it is probable that there is a branching in the chain of disintegration. This is known to be true for RaC, AcC, and ThC. The radiation which leads to the product in the side-chain is represented in brackets. (See Tables 6, 7, and 8.) In the cases of Ra, RdAc, and RdTh, experimental work has not yet settled whether the expulsion of the β -particle (which is of much less importance in all three bodies than the expulsion of the α -particle) leads to the formation of a side-chain.

The Group-Displacement Law has simplified experimental work in some ways, and chiefly in two :

(1) It has led to the discovery of a few elements in those cases in which the disintegration series as set out in 1913 contradicted the law. Two may be given as examples :

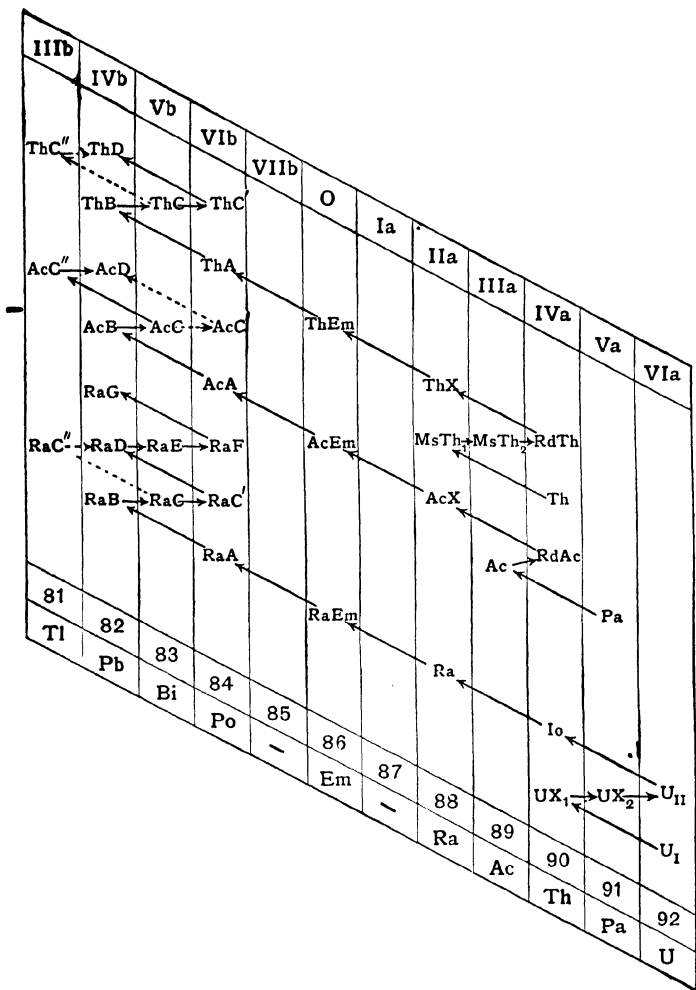
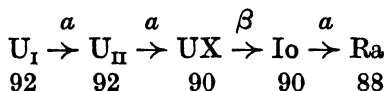
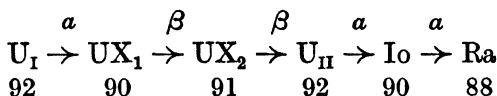


FIG. 8.—THE RADIO-ELEMENTS AND THE PERIODIC SYSTEM.

(a) Before 1913 the uranium series was supposed to commence thus :



which, as is seen, contravenes the law in two cases out of four. If now the series be written

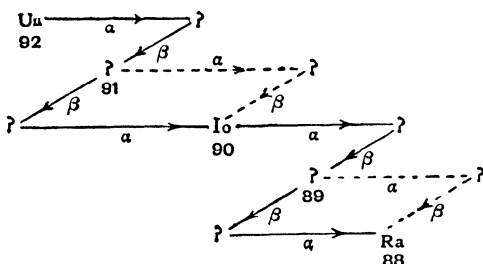


the difficulties are overcome. This is the only way in which the series may be written to fit in with the law. It postulates the existence of a new body, UX_2 , which is the product of UX_1 , and which expels β -particles. As a result of this scheme this new body was discovered by Fajans. It was found to be the direct product of UX_1 , and to expel β -particles.

(b) Again, since the At. No. of actinium is 89, its parent must have an At. No. of 91 if the parent expels an α -particle, or 88 if it expels a β -particle. Now Ra has At. No. 88, and it expels a β -particle (in addition to an α -particle), so that it is a possible parent of actinium. Chemical work, however, showed that this view is untenable. No other body with this atomic number is a possible parent. The parent, therefore, *must have* an At. No. of 91, *i.e. must be* the homologue of Ta. Experiment justified this view. Some tantalum in solution was added to a uranium mineral in solution, and the tantalum separated from the other metals. It contained a substance from which actinium was pro-

duced in time. This substance is the parent of actinium.

(2) It has excluded the possibility of the existence of undiscovered elements between supposedly successive products. For example, when ionium was discovered, its relationship to uranium in the disintegration series was not accurately known. In the example above, it is shown that it must be the product of uranium II, and the parent of radium. If β -particle products existed between uranium II and ionium, and between ionium and radium, the only possible schemes are indicated in the diagram below.



Each scheme would make the atomic weight of Io eight less than that of U_{II} , and that of Ra eight less than that of Io; both of which suppositions are contrary to fact. It follows that there cannot be β -particle products either between U_{II} and Io or Io and Ra.

CHAPTER VII

ISOTOPES

IN the last chapter it has been shown that, by fitting the members of the three disintegration series into their places in the periodic system, the surprising result was arrived at that several elements occupied the same place in the periodic system. These elements are called isotopes, and so far they have been described as "similar" chemically to a type element. It will be shown in this chapter that experimental work proves that *all occupants of the same place in the periodic system are not merely similar to the type element in chemical properties, but are identical with it.* This is a statement of great consequence.

Short account of the development of the subject.

—The first radio-elements to be discovered, uranium and thorium, occupied unmistakable positions in the periodic classification. Polonium, radium, actinium, and the radium-emanation, the next four to be discovered, were found to be the true occupants of places which had previously been marked by blanks. Six elements were thus fitted in without difficulty. But as more and more radio-elements were discovered, difficulties arose. There were three different emanations, for example, and but one place for a gas of the inert

group. One or two workers, assuming from rather poor evidence that actinium's atomic weight was about 160, attempted to fit the members of the actinium series into the numerous blank spaces in the region of the rare-earth elements which were shown in the diagrams of the periodic classification of that period. Most workers who considered the matter, however, could not escape from the conclusion that the majority of the radio-elements were "outside the periodic system," just as are (it is believed at present) the group of rare-earth elements.

McCoy and Ross in 1907 were the first to point out that many radio-elements could not be separated from each other or from some common elements by chemical means. This suggested similarities in chemical properties. The similarity of the element ionium, isolated by Boltwood in 1907, to thorium was studied in detail by Boltwood and later by Marckwald and Keetman. Boltwood found that if compounds of these two elements got mixed in the course of his work, the two kept together, and did not allow themselves to be separated by any chemical process he had occasion to put them through. The question did not arise: Is the separation of ionium from thorium a difficult one of the same order as the difficulty, say, of a rare-earth separation, or is it very much more difficult? And the subject was not pursued.

In 1907 the problem was taken up by Marckwald and Keetman. Like Boltwood, they found ionium and thorium very similar in their chemical properties, but they concluded, after two years' fruitless attempt to concentrate one even in the least degree in a mixture

of both, that ionium and thorium not merely resemble one another in a remarkable way, but do not in fact differ at all in any of their chemical properties. This was a remarkable conclusion, and the question arose : Is this really so, or is it simply a confession of failure ? Every conceivable chemical method was tried by these two men. To detect the slightest change they had the physical apparatus of radio-activity at their disposal, electroscopes which for radio-active bodies are many thousands of times more sensitive in detecting a change of concentration than any that could be used for the rare earths, yet change there was none. This was a most important result, and Marckwald must be regarded as the pioneer in this work on isotopes.

Hahn, a little later than this, showed that radio-thorium was non-separable from thorium itself, and that both had identical chemical properties. If Marckwald and Keetman's result is combined with Hahn's, it is seen that thorium, ionium, and radio-thorium are all non-separable, *i.e.* are isotopes. This is important in showing that isotopy is not confined to two elements only.

Hahn showed also that mesothorium 1, which he discovered, radium and thorium X were also isotopes. Other workers confirmed and extended these results. It soon became obvious that from general similarities radium A, actinium A, and thorium A, should be isotopes, the group of B bodies also, and the group of C bodies, and the group of D bodies. Again, the thorium series appeared to resemble the actinium series more closely than the radium series, notably in that both possessed four disintegration-products only

after the emanation. It was surmised, therefore, that thorium X would be similar chemically to actinium X, and radio-thorium to radio-actinium. These predictions were shown experimentally to be true. Notable workers in this field were v. Hevesy, who showed that members of certain groups had identical electrochemical properties, Fleck, who made a systematic investigation of the purely chemical properties, Svedberg and Strömholm, Soddy, and Fajans. In a short time every radio-element, including the end-products, except one or two of very short half-value period, had been investigated and placed among its isotopes.

Radio-active isotopes.—The full list is given at this stage for reference. It supplements the facts of Fig. 8, with additional information :

TABLE 10.—LIST OF ISOTOPES

<i>Atomic Number.</i>	<i>Type.</i>	<i>Group in Periodic System.</i>	<i>Isotopes.</i>	<i>At. Wt.</i>
81	Tl	III B	Tl	204.0
			AcC''	(206)
			ThC''	208
			RaC''	210
82	Pb	IV B	Pb	207.2
			RaG(Pb _G)	206
			AcD(Pb _{Ac})	(206)
			ThD(Pb _{Th})	208
			RaD	210
			AcB	(210)
			ThB	212
			RaB	214

TABLE 10 (*continued*)

<i>Atomic Number.</i>	<i>Type.</i>	<i>Group in Periodic System.</i>	<i>Isotopes.</i>	<i>At. Wt.</i>
83	Bi	V B	Bi	209·0
			RaE	210
			AcC	(210)
			ThC	212
			RaC	214
84	Po	VI B	Po	210
			AcC'	(210)
			ThC'	212
			RaC'	214
			AcA	(214)
			ThA	216
			RaA	218
85	[Eka-Iodine]	VII B	—	—
86	Em	O	RaEm	222
			AcEm	(218)
			ThEm	220
87	[Eka-Cæsium]	I A	—	—
88	Ra	II A	Ra	226·0
			AcX	(222)
			ThX	224
			MsTh 1	228
89	Ac	III A	Ac	(226)
			MsTh 2	228

TABLE 10 (*continued*)

<i>Atomic Number.</i>	<i>Type.</i>	<i>Group in Periodic System.</i>	<i>Isotopes.</i>	<i>At. Wt.</i>
90	Th	IV A	Th	232.2
			RdAc	226
			RdTh	228
			Io	230
			UY	(230)
			UX ₁	234
			UZ	234
91	Pa	V A	Pa	(230)
			UX ₂	234
92	U	VI A	U _{II}	234
			U _I	238.2

Isotopes, then, have by definition the same position in the periodic classification, *i.e.* the same atomic number. They possess also, as has been found experimentally, identical chemical properties. But they differ in radio-active properties, and they may differ in atomic weight. Before this represented the full state of knowledge the question arose: Do isotopes possess any identical physical properties? After the publication of Marckwald's work, and before that of the workers mentioned above, the writer came to the conclusion that isotopes probably possessed identical physical properties except those of radio-activity and atomic weight. To commence an attack on this problem Rossi and the writer investigated the arc spectrum of preparations of thorium and its isotope

ionium. They showed that it was impossible to detect a difference in the arc spectra of pure ThO_2 , and of a mixture of ThO_2 and IoO_2 , containing approximately 20% of the latter in circumstances such that an impurity of $1\frac{1}{2}\%$ of a body of high atomic weight was easily detected. From these experiments they concluded that the arc spectra of thorium or ionium were identical, and they generalised this result to include all isotopes. Since then these results have been confirmed, and numerous investigations have been made of many of the physical properties of different groups of isotopes.

Different and identical properties of isotopes.

—As a result of these experiments, isotopes have been found to differ in the following properties :

(1) Radio-activity.

(2) Atomic weight.

(3) Properties which depend upon atomic mass, such as density and solubility expressed in grams per c.c. or per litre.

These may be called individual properties. Isotopes have been found to be identical in the following properties :

(4) Atomic number and X-ray spectrum.

(5) Chemical properties.

(6) Arc spectrum.

(7) Atomic volume, molecular solubility, density expressed in moles per litre.

(8) Volatility.

(9) Melting and freezing points.

(10) Electro-chemical potential.

(11) Diffusion velocity of ions in solution.

(12) Refractive index.

(13) Magnetic susceptibility, and others.

These may be called type properties.

Each of these thirteen properties has not been specifically investigated in every isotope, but sufficient experiments have been done to render it very probable that what is experimentally proven for such isotopes as have been examined holds throughout.

Typical examples of the results obtained will now be given.

(1) *Radio-activity*.—The differences in the radio-activity of isotopes are very striking. Consider the isotopes of thorium (see p. 77). Four of the isotopes expel α -particles only, and three β -particles. The initial velocities of both these kinds of particles is characteristic of each isotope. The half-value periods are all different, and the difference between some is very great.

(2) *Atomic weights*.—The most conclusive experimental evidence with respect to differences in atomic weights is obtained from a study of the isotopes of lead (see below), but the evidence is good for all other sets of isotopes.

Consider the three emanations. The atomic weight of RaEm is $226.0 - 4.00 = 222.0$; that of ThEm $232.2 - 3 \times 4.00 = 220.2$, since 226.0, 232.2, and 4.00 are the experimental values of the atomic weights of radium, thorium, and the α -particle respectively.

Consider the isotopes of thorium again. The atomic weight of Th is 232.2; that of RdTh is 4 less, *i.e.* 228.2; that of Io $4 + 226 = 230$ calculated from radium, or $238.2 - 8 = 230.2$ calculated from

uranium I; that of RdAc is $234 - 4 = 230$, or $230 - 4 = 226$, depending upon which of the two possible values of the atomic weight of protactinium is selected; that of uranium X is $238.2 - 4 = 234.2$.

It may be seen from Table 10 that 8 is the maximum difference in the atomic weights of radio-active isotopes.

The atomic weights of the three leads will now be considered.

The three "leads."—The atomic weight of ordinary lead is 207.2. That of RaG, the end-product of the uranium series, should be 206.0, assuming that of Ra to be 226.0, and that of the α -particle (a helium atom) 4.00, since five α -particles are expelled in the change of Ra into RaG.

Hönigschmid and Horovitz showed that lead separated from a specimen of pitchblende from German East Africa had an atomic weight of 206.05, and that from a specimen of bröggerite, 206.06. Richards and Wadsworth found the lead separated from cleveite had an atomic weight of 206.08, and that from his specimen of bröggerite 206.12. The three minerals from which the lead was separated are primary minerals containing uranium, but no thorium, so that the lead they contain consists of RaG with perhaps a small quantity of ordinary lead, and is not contaminated with the end-product of the thorium series. The close agreement between 206.0, the calculated result, and the lowest of those found experimentally is remarkable.

The atomic weight of ThD, the end-product of the thorium series, should be 208.12, since that of thorium is 232.12 and six α -particles are expelled in the disintegration of the latter into the former.

It is not possible to obtain a thorium mineral free from uranium, so that the lead in the mineral always contains both RaG and ThD. As the atomic weight of the former is 206·0, its presence makes the mean atomic weight of the mixture diverge from atomic weight of ThD to an extent depending upon the ratio of RaG to ThD in it. Below are tabulated the atomic weights of lead from thorium minerals containing different relative amounts of thorium and uranium.

<i>Mineral.</i>		% <i>Th.</i>	% <i>U.</i>	% <i>Pb.</i>	<i>At. Wt.</i>
Thorianite	.	57·0	26·8	3·5	206·83
„	.	62·7	20·2	3·1	206·90
„	.	68·9	11·8	2·3	207·21
Thorite	.	30·1	0·45	0·35	207·90

It is seen from this table that as the amount of thorium in the mineral relative to that of uranium rises, the atomic weight of the lead increases. The specimen of thorite for which the data are given here contains the highest ratio of thorium to uranium known. Its lead, therefore, is freest from RaG. The atomic weight of this, 207·9, is not very different from that to be expected theoretically in a mineral which contains ThD free from its isotopes.

There are thus three leads, each with its own atomic weight, found in nature in sufficient amount for all their chemical and physical properties to be investigated by ordinary methods.

Ordinary lead, at. wt. 207·2.

RaG, or uranium lead, at. wt. 206·0.

ThD, or thorium lead, at. wt. 208·1.

(3) *Properties depending upon atomic mass.*—(a) The density of lead of different atomic weights has been determined at 19·94° by Richards and Wadsworth. Their results are given in the following table :

Atomic weight of lead	206·085	206·34	207·20
Density	11·273	11·288	11·337
Atomic volume	18·281	18·280	18·276

It is seen that the densities of the three isotopes are proportional to their atomic weights, and consequently different. The atomic volumes do not vary more than the experimental error.

(b) The solubility of a solution expressed in grams per litre.

Richards and Schumb found that at 25° C. a saturated solution of lead nitrate contained 595·95 grams $\text{Pb}(\text{NO}_3)_2$ for 1,000 grams of water for $\text{Pb} = 207·19$, and 594·28 grams for $\text{Pb} = 206·34$. Fajan's and Lemberg found that 10 c.c. of a saturated solution of lead nitrate at 24·45° C. weighed 14·4450 grams for $\text{Pb} = 207·20$ and 14·4359 grams for $\text{Pb} = 206·59$.

The molecular solubilities of the two specimens of lead in both these experiments, however, were equal within experimental error. Thus Richards and Schumb found in their experiments that 1·7993 moles of $\text{Pb}(\text{NO}_3)_2$ were associated with 1,000 grams of water in a saturated solution of lead nitrate at 25° C. for $\text{Pb} = 207·19$, and 1·7989 moles for $\text{Pb} = 206·34$, an agreement of 4 in 18,000.

(4) *X-ray spectrum.*—The two strongest lines in the L series of lead (the so-called α and β lines) were

photographed by Siegbahn on the same plate and under the same conditions for two specimens of lead, one of atomic weight 207·2, the other 206·05. The wavelength of the lines agreed to 0·0001 Å unit.

Rutherford and Andrade showed that the characteristic X-radiation of lead (207·2) has the same wavelength as the γ -radiation emitted by its isotope radium B (214).

(6) *Arc spectrum*.—Aronberg and Merton examined the line 4058 Å in the spectrum of two specimens of lead, one 207·2, the other 206·0 in atomic weight. They found a difference of 0·0044 Å only, or about 1 in 10^6 of the absolute value. For thorium lead (mainly ThG) and ordinary lead the difference in wave-lengths of the line 5350 Å in the two has been found to be 0·0055 Å, or about 1 in 10^6 .

The failure to detect differences between the spectra of ionium and thorium has been mentioned already. The conclusion from these and other experiments is that arc spectra of isotopes differ genuinely, but by so very little that for practical purposes they may be said to be identical.

(7) Atomic volume has been mentioned under (3).

(8) *Volatility*.—Marckwald and Keetman found that the ratio of the amount of thorium to ionium in a preparation was not altered in the least by volatilisation. Paneth and v. Hevesy came to a similar negative result with regard to the volatility of radium D and lead.

(9) *Melting and boiling points*.—Richards and Hall found that the melting points of lead 206·4 and of lead 207·2 did not differ by more than 0·05° C. The same

authors found also that the thermo-electric properties of wires of the same two leads were identical. Bridgman found that there was no difference in the conductivities of the same two samples, nor in the effect of pressure and temperature upon the conductivities.

Isotopes and the nuclear theory of the atom.

—From Rutherford's nuclear theory of the atom the existence of isotopes may be simply deduced. The chief point of the theory necessary for this purpose is that the charge on the nucleus conditions the chemical properties of the atom, the mass of the nucleus having an influence which must be very small. Hence atoms whose nuclei have the same charge have the same chemical properties. Now it is possible for nuclei to have different compositions and yet possess identical charges, since the charge (which is positive) is a net one, being the algebraic sum of the positive and the negative charges which the nucleus contains; the number of charges may vary so long as their algebraic sum is constant.

A nucleus with a given charge may consequently have various compositions. Hence it is that isotopes have different radio-active properties, for radio-activity, being a property of the nucleus, must be a function of its composition. The differences in atomic weights which isotopes show may also be deduced. Consider an atom whose nucleus contains p positive and n negative charges. Its net charge, *i.e.* its atomic number, is $p - n$. A second atom whose nucleus has $p + 2$ positive and $n + 2$ negative charges, and a third atom whose nucleus has $p + 4$ positive and $n + 4$ negative charges, have the same atomic number as the first. The three

are consequently isotopes, but it is obvious that their atomic weights are different, since a difference of one unit in the gross amount of positive electricity is equivalent to two units of atomic weight.

It appears, however, that, although many are possible, certain compositions of the nucleus alone are stable, for few are found to exist. Experimentally, it is found that the maximum variation in the gross amount of positive electricity in the nucleus is four charges, corresponding to eight units of atomic weight.

Examples.—Thorium loses two positive and two negative charges (four units of mass) in its transformation into its isotope radio-thorium; so for uranium I into uranium II. Radium B loses two positive and two negative charges (four units of mass) in changing to radium D, and four positive and four negative charges (eight units of mass) in changing to radium G.

Separation of radio-active isotopes.—It has been said elsewhere that no radio-active isotopes have yet been separated completely, nor has even a concentration of one in a mixture been effected. The problem appears less difficult, however, when the isotopes of the common elements are considered. For their separation the following methods have been suggested: by diffusion, by thermal diffusion, by gravitation or “pressure diffusion,” by evaporation at very low pressure, by positive rays and by photochemical methods. A few positive results have been obtained, notably by v. Hevesy and Brönsted on the isotopes of mercury and by Harkins on the isotopes of chlorine. The subject, however, is still in its infancy.

REFERENCE.—Dr. F. W. Aston: *Isotopes* (Arnold, 1922).

CHAPTER VIII

DESCRIPTION OF THE TYPES OF RADIO-ELEMENTS

THE ten type elements, with their atomic numbers and atomic weights and group in the periodic classification, are given in the following table :

TABLE 11

<i>At. No.</i>	<i>Element.</i>	<i>Symbol.</i>	<i>At. Wt.</i>	<i>Group.</i>
92	Uranium . . .	U	238.2	VIA
91	Protactinium . . .	Pa	(230)	VA
90	Thorium . . .	Th	232.1	IVA
89	Actinium . . .	Ac	(226)	IIIA
88	Radium . . .	Ra	226.0	IIA
87	—			IA
86	Radium emanation . . .	RaEm	222	0
85	—			VIIB
84	Polonium . . .	Po	210	VIB
83	Bismuth . . .	Bi	209.0	VB
82	Lead . . .	Pb	207.2	IVB
81	Thallium. . .	Tl	204.0	IIIB

Bismuth, lead, and thallium, being well-known elements, are not described here. The primary elements, uranium and thorium, will be described later (Chapters IX and X) in more detail than the others.

91 PROTACTINIUM Pa (230): Group VA

(a) *Discovery*.—It was known that actinium is in some way a branch-product of uranium, and, since its atomic number is 89, the atomic number of its parent must be either 91 or 88, according as the parent emits an α - or a β -particle. In the former case the parent of actinium should be similar to tantalum. A soluble tantalum salt was therefore added to a large quantity of pitchblende residues, and when separated out and purified was found to contain a body which on disintegration gave actinium. This body was therefore the parent of actinium and was named protactinium by Hahn and Fr. Meitner, who discovered it in this way in 1917. The existence of this body was also proved by Soddy and Cranston, who heated pitchblende in an atmosphere of carbon tetrachloride under conditions in which Ta_2O_5 was volatilised. Actinium appeared gradually in the sublimate, which therefore contained its parent element.

(b) *Occurrence*.—Protactinium occurs only in uranium minerals.

Its relation to uranium has been discussed on p. 54.

Protactinium, therefore, is not really a primary radio-element, but for purposes of classification, and because of lack of knowledge with regard to its relation to uranium, it is convenient to class it so.

The atomic weight of Pa has been discussed on p. 56. It is taken as 230. This fixes the atomic weights of all the products of the actinium series.

The point may be settled when the atomic weight of protactinium may be, but has not yet been, directly

determined. This is possible because it has a long half-value period and consequently exists in weighable quantity.

(c) *Extraction*.—Protactinium has been removed from pitchblende residues in the following manner. The residues are boiled for a long time with nitric acid. Most of the radio-active constituents present, including radium, go into solution. A little tantalum oxide and a few milligrams of thorium and lead nitrates are then added to the residue, and the whole extracted with hydrofluoric and sulphuric acids. The tantalum and protactinium go into solution; the thorium and lead, and with them UX_1 , Io , and RaD , remain insoluble. The solution is evaporated to dryness and ignited, and compounds of iron, zirconium, etc., may be removed from the insoluble tantalum and protactinium by boiling with aqua regia. So far tantalum and protactinium have not been separated.

(d) *Chemical properties*.—Nothing is definitely known at present about its chemical properties, except that it resembles tantalum, of which it is evidently the homologue.

89 ACTINIUM Ac (226): Group IIIA

(a) *Discovery*.—Debierne in 1899, while working up uranium residues, discovered an element which was precipitated from solution by ammonia, and yet was distinct in its radio-activity from thorium. This he called actinium. Giesel in 1902 separated from pitchblende a very active substance along with the rare earths, and after further fractionation he found the new body was associated with lanthanum. He called

it emanium as it gave, like radium, an emanation. Emanium and actinium were later shown to be the same.

(b) *Occurrence*.—Actinium, like its parent protactinium, occurs in uranium minerals and there only.

(c) *Chemical properties*.—The chemical properties of actinium resemble those of the rare earths, and are generally similar to those of lanthanum, but when fractionated along with rare earths, it appears to be concentrated in the neodymium and samarium fractions, so that it would occupy a position in the serial order of the rare-earth elements between these two elements, viz. 57 La, 58 Ce, 59 Pr, 60 Nd, **Ac**, 62 Sm, 63 Eu, 64 Gd, etc., i.e. it appears to be a homologue of the missing element of atomic number 61.

Other experiments have shown that it is intermediate between lanthanum and calcium in chemical properties. In qualitative analysis it is precipitated as hydroxide by ammonia, but quantitatively only in absence of ammonium salts; its oxide is therefore more strongly basic than that of aluminium. It is precipitated as oxalate by oxalic acid or by ammonium oxalate, but not quantitatively when free mineral acids are present. In this respect it resembles lanthanum. It is not precipitated from the solutions of the chlorides by sodium thiosulphate, nor from a solution of nitrates by hydrogen peroxide, so that it is easily separated from thorium. Like the rare earths, it is precipitated quantitatively by aqueous hydrofluoric acid in excess. It is precipitated along with manganese when that element is precipitated from basic solutions as manganite.

Actinium has not yet been prepared free from rare earths. Because of this difficulty, but much more because of its relatively short half-value period, it is doubtful whether a quantity large enough for an atomic weight determination or a spectroscopic examination could be extracted from minerals.

88 RADIUM Ra (226.0): Group IIA

(a) *Discovery*.—In their pioneer work on radio-activity in 1898, M. and Mme Curie found that radio-active minerals containing uranium were several times more active than they would have been if their radio-activity had been due to uranium alone, even if the mineral had contained nothing but pure uranium compounds. They had found experimentally that radio-activity was an atomic property, and they proved that no special combination of uranium with other elements could increase the radio-activity in any way. It was therefore deduced that other and more powerfully radio-active substances were present in pitchblende. The mineral was put into solution and analysed qualitatively in the ordinary manner, each precipitate being examined for new radio-active bodies by the methods of radio-activity. A substance now known as radium was found with the barium of the mineral, and another, polonium, with the bismuth.

(b) *Occurrence*.—Radium, being a disintegration product of uranium, occurs in uranium minerals only, and provided the minerals are sufficiently old, and that they have not been weathered, in a constant ratio to the amount of uranium of approximately 3.4×10^{-7} to 1 (the ratio of the half-value periods),

the calculation applying to both substances in the elementary form. In 3 tons of uranium there is approximately 1 gram of radium. Radium is found in this ratio (the equilibrium ratio) in old minerals like carnotite, pitchblende, and thorianite, but not in more recent minerals like autunite, where the amount varies from 75% to 20% of the equilibrium amount only. Carnotite, a hydrated vanadate of potassium and uranium, $K_2O \cdot 2UO_2 \cdot V_2O_5 \cdot 3H_2O$, is the chief source of radium. It is found in largest quantities in Colorado and Utah. Pitchblende or uraninite, which consists of U_3O_8 with PbO , Fe_2O_3 , and traces of ThO_2 , rare earths, etc., is also an important source.

(c) *Extraction*.—Radium is extracted from minerals in two stages :

(i) The barium of the mineral is separated from a solution, or is separated from its residues by the usual chemical methods. If the mineral contains little or no barium, a small quantity of a soluble barium salt is added to it, and the barium is later separated out. The whole of the radium associates itself with the barium, which it resembles very closely.

(ii) As there is no reagent yet found which precipitates one of these elements quantitatively, leaving the other in solution, radium is separated from barium by fractional crystallisation. The usual salts employed are the chlorides and the bromides. The halogen salts of radium are less soluble in water and mineral acids than the corresponding salts of barium. The hydroxide of barium, however, is less soluble than that of radium, and a separation based on fractional precipitation of barium hydroxide from a solution containing

barium and radium salts has been patented. The picrates, bromates, and ferrocyanides have been proposed also as suitable salts for fractionation. In laboratory work crystallisation of the chlorides is considered the most satisfactory process.

In extracting radium from carnotite, it has been found that if the ore be boiled with 96%, 78%, and 35% sulphuric acid, the percentages of the total radium which go into solution are 95, 92, and 42. In actual work 10 kilos of ore are gradually added to 18 kilos of 78% sulphuric acid heated to 190°, and after a thorough mixing the whole is filtered. The residue is washed twice with fresh hot acid, and the filtrate and washings are run into eight times its volume of hot water and well stirred. The sulphates of radium and barium are thus thrown out of solution and filtered off from other constituents of the ore. After further purification the mixed sulphates are prepared for the process of fractional crystallisation. In the complete process from 85% to 95% of the radium in the mineral may be recovered.

(d) *Metallic radium* has been prepared by a method similar to that employed by Guntz in the preparation of metallic barium.

Liquid radium-amalgam was prepared by electrolysis about 0.1 gram of radium chloride with a mercury cathode. The amalgam was distilled in hydrogen under reduced pressure. At 700° the last of the mercury was volatilised, leaving the radium as a pure white metal which melts at about 700°.

(e) *Compounds of radium*.—The chief compounds of radium are :

Radium hydroxide	. $\text{Ra}(\text{OH})_2$
„ chloride	. RaCl_2 and $\text{RaCl}_2 \cdot 2\text{H}_2\text{O}$
„ bromide	. RaBr_2 and $\text{RaBr}_2 \cdot 2\text{H}_2\text{O}$
„ nitrate	. $\text{Ra}(\text{NO}_3)_2$
„ sulphate	. RaSO_4
„ carbonate	. RaCO_3

The chemical properties and appearances of these compounds are very similar to those of the corresponding barium salts. The sulphate, the hydrated chloride, and the hydrated bromide are the commonest.

$\text{RaCl}_2 \cdot 2\text{H}_2\text{O}$ is less soluble in dilute hydrochloric acid than $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$; and $\text{RaBr}_2 \cdot 2\text{H}_2\text{O}$ in dilute hydrobromic acid than $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$. The carbonate dissolves readily in hydrochloric acid. At 25° the solubility of the sulphate in water is 2.3×10^{-8} grams per c.c. (compare that of BaSO_4 , 2.3×10^{-6} grams per c.c.).

A separation of radium from barium based on the difference in solubility of their sulphates has been found to be impossible, owing to isomorphism. The sulphate precipitated from a solution of both substances consists of mixed crystals of the two bodies in the ratio they are present in the solution.

The action of the radiations emitted by radium must not be forgotten when preparing its salts. The bromide, when exposed to air, gives off bromine and is ultimately changed to carbonate. The water in a moist preparation is decomposed gradually into its elements, and if such a preparation be sealed up, an accident may result. The safest preparation to deal with is the sulphate, since it is stable, anhydrous, and

can be kept dry. If a radium-solution is required to be made from the sulphate, the latter is best decomposed by fusion with alkaline carbonates, and the well-washed radium carbonate which results dissolved in hydrochloric acid free from sulphuric acid.

Another method has been suggested, namely to reduce RaSO_4 to RaS by fusion with sugar charcoal, and to dissolve the sulphide in pure hydrochloric acid. The writer has found the carbonate method much the better. It is, of course, the usual laboratory method for converting barium sulphate into the chloride.

The arc spectrum of radium is very characteristic, and is that to be expected from the highest member of the alkaline earth series of elements.

Salts of radium colour the bunsen flame carmine.

Hönigschmid's determination of the atomic weight is considered the most accurate. He made a careful determination of the ratio of RaCl_2 to RaBr_2 . The value he found was 225.97.

(f) *Estimation of radium*.—Radium is usually estimated by comparing it with a standard radium preparation of 100% (or of known) purity in one of two ways.

(1) *By the γ -ray method*.—This is suitable for comparing quantities of radium from 10^{-5} gram up to several grams.

(2) *By the emanation method*.—This is suitable for measuring quantities of radium from 10^{-10} to 10^{-5} gram.

THE γ -RAY METHOD

This method of measurement depends on the fact that the radium in a radium salt one month after its preparation is in equilibrium with its products, and emits penetrating γ -rays whose intensity is proportional to the amount of radium present. The intensity of the γ -radiation from the radium to be tested is compared, in an electroscope, with that due to a preparation whose content of radium is accurately known. The electroscope should have its walls and base made of lead at least 3 millimetres thick, so that only γ -rays are able to enter and produce ionisation. A standard radium preparation of known content in a thin glass tube is placed at a convenient distance from the electroscope, and the rate of discharge of the gold-leaf measured. The preparation to be compared is sealed in a similar tube, placed at exactly the same distance from the electroscope, and the rate of discharge measured. It is obvious that the most accurate results will be obtained when the rates of discharge are not widely different. In a laboratory there is often a series of standards in the ratio, approximately, of 1, 10 and 100, so that, after a preliminary measurement, the unknown may be compared accurately with the standard nearest in strength to it.

THE EMANATION METHOD

The principles on which the emanation method depend are these :

- (1) If a radium solution be freed from emanation by boiling, and be then sealed up in a vessel, the emana-

tion present reaches its equilibrium value in one month ; or it reaches a known fraction of this equilibrium value in any time less than a month. This fraction $f = \frac{Q_t}{Q_\infty} = 1 - e^{-\lambda t}$ * where Q_t is the quantity at any time t , and Q_∞ is the maximum (the equilibrium) quantity, and $\lambda = 0.75$ per hour, the time being expressed in hours.

(2) The equilibrium amount of emanation is proportional to, and therefore a measure of, the quantity of radium.

(3) The emanation can be completely expelled from the solution into an electroscope with an air-tight chamber at atmospheric pressure.

(4) About four hours after the emanation has been introduced into the electroscope, its products, RaA, RaB, and Ra(C + C' + C''), reach their maximum value, and the ionisation due to the emanation and its products, measured by the rate of fall of the gold-leaf, remains sufficiently constant for accurate measurements to be made. The ionisation at this time is taken as a measure of the emanation present, and therefore of the radium.

(5) The operations described above are carried out first with a radium solution of known strength, and later with the unknown radium solution, and the strength of the latter is calculated in terms of the former from the electroscopic readings.

For this work a standard radium solution may be prepared in two ways :

* This function has been evaluated for different hours and days. The table of values is given in *Rutherford*, p. 665.

(a) A quantity of radium salt is accurately determined by the γ -ray method in terms of the radium standard. Suppose the radium salt contains 1 milligram of radium. This radium salt is dissolved in water and some hydrochloric acid added to ensure complete solution. The solution is then diluted to a known volume, say 1 litre. A definite fraction of this solution, say 1 c.c., is accurately removed and again diluted to a litre. One cubic centimetre of the last solution contains 10^{-6} milligram of radium. This serves as a convenient standard radium solution, for it gives a suitable rate of discharge of the gold-leaf in the emanation-electroscope.

(b) A homogeneous quantity of pitchblende is carefully analysed for uranium. Assuming that the radium in the mineral is present in equilibrium amount, and that the ratio of the quantity of uranium to that of radium is known, it is possible to calculate the amount of radium present in a given weight of the mineral from its uranium content. As the first of these assumptions is justifiable in the case of pitchblende, and as the ratio of uranium to radium is accurately known, a quantity of pitchblende makes a convenient and cheap standard of radium. It need not be put into solution until the day on which the standardisation is being carried out. This prevents any precipitation of the radium, and hence occlusion of a part of the emanation, which is apt to occur in solutions which are kept for some time. The mineral is obtained in solution when required by dissolving it with concentrated sulphuric acid in presence of a few crystals of KNO_3 or a few drops of HNO_3 .

In practice an experiment is carried out as follows : Thirty milligrams of pitchblende are weighed out accurately into a vessel of the shape shown in Fig. 9. Add a few drops of HNO_3 and then 15 c.c. of concentrated H_2SO_4 through funnel. Close tap A. Heat B gently with flame for ten minutes ; acid fumes come off

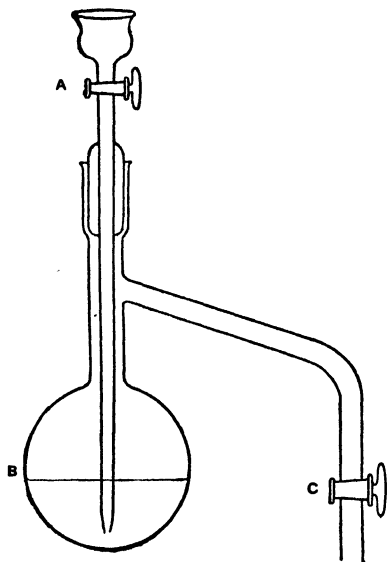


FIG. 9.

copiously. Open A a little so that a gentle stream of air bubbles through the solution. The expelled emanation, the acid fumes, and the air are collected in a gas-holder over a strong solution of CaCl_2 (in which the emanation is almost insoluble) attached to the apparatus below C. This is rejected, and the taps A and C closed.

Three or four days later (the exact number of days and hours must be noted) the solution in the vessel is again completely boiled out as before into the gas-holder. When the gas in the gas-holder has cooled, and the acid fumes dissolved in the solution, it is transferred to an evacuated electroscope of the type shown in Fig. 10, through a tube of calcium chloride

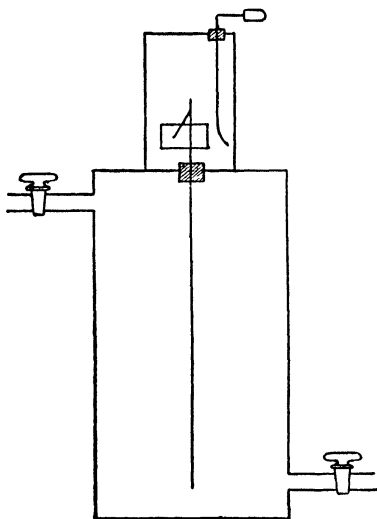


FIG. 10.—Emanation Electroscope.

to dry the gas. The volume of the electroscope must, of course, be greater than that in the gas-holder. The gas in the electroscope should contain the whole of the emanation produced by the radium in the pitchblende in the few days that it has been sealed up. The gas is brought to atmospheric pressure and the taps of the electroscope closed. The central rod of

the electroscope is now charged to — 200 volts so that the RaA, RaB, and Ra(C + C' + C'') produced by the emanation will definitely settle upon it instead of distributing themselves throughout the volume of the gas. After four hours the ionisation is a maximum, and the rate of discharge of the gold-leaf electroscope is carefully noted. Finally the electroscope is exhausted, and replenished with air several times to remove the emanation completely.

The unknown solution is then treated in the same way, and the emanation introduced into the same electroscope and the ionisation determined after four hours.

Example.—A radium solution of unknown strength was freed from emanation, sealed up for four days eight hours, its emanation then removed, and the ionisation measured in the manner given above. The rate of discharge of the gold-leaf was 35 scale divisions per minute.

A few days later 30 milligrams of pitchblende, containing 70% U_3O_8 , was freed from emanation, sealed up for three days nine hours, the emanation then removed, and the ionisation measured in the same electroscope. The rate of discharge of the gold-leaf was found to be 20 scale divisions per minute. The pitchblende contained $30 \times .7 \times .848 \times 3.4 \times 10^{-7}$ milligrams of radium because .848 is the factor to reduce U_3O_8 to U, and 3.4×10^{-7} to reduce a unit of uranium to the same unit of radium. The quantity of emanation that was produced by this quantity in three days nine hours is only .455 of the equilibrium amount. Therefore

$\cdot 455 \times 30 \times \cdot 7 \times \cdot 848 \times 3\cdot 4 \times 10^{-7}$ milligrams of radium in equilibrium, *i.e.* after a month's sealing up, would give the same ionisation effect, *i.e.* 20 scale divisions per minute. One scale division therefore corresponds to $1\cdot 377 \times 10^{-7}$ milligrams of radium.

Now in the unknown solution only $\cdot 542$ of the equilibrium amount had accumulated in four days eight hours. Let it contain x milligrams of radium, then $\cdot 542x$ corresponds to 35 scale divisions, *i.e.* $35 \times 1\cdot 377 \times 10^{-7}$ milligrams of radium. Hence x .

86 RADIUM EMANATION RaEm (222): Group 0

(a) *Discovery*.—Early workers in radio-activity found that all bodies in the neighbourhood of a preparation of radium, or of thorium, or of actinium, became themselves radio-active. Several theories of this “excited activity” (as it was called) were put forward. It was shown by Dorn in 1900 that the “excited activity” was due to disintegration products from a radio-active gas which was generated continuously by radium, for if the radium preparation were sealed up so that the gas could not escape, bodies in the neighbourhood were no longer excited into activity. The same theory was found to hold for the emanations from thorium and actinium.

Rutherford and Soddy in 1903 showed that the radium emanation resisted all attempts to enter into chemical combination, and was indeed the missing homologue of the group of inert gases.

The emanation, being a member of this group, has no chemical properties. Its physical properties apart from its radio-activity are those to be expected from

its position in the periodic classification. As it has the longest half-value period of the three emanations, it has been most studied. It has a density of 111; it boils at -65° ; its critical temperature is 104.5° ; its absorption-coefficient in water is 0.30; its coefficient of diffusion (in $\text{cm.}^2 \text{sec.}^{-1}$) into air at N.T.P. is 0.1. It has a characteristic spectrum.

The amount of emanation in equilibrium with 1 gram of radium (element) has been both determined experimentally and calculated by Rutherford and found to be 0.59 c.mm. A volume of emanation of this order has been both weighed and its density determined by Ramsay and Gray with a microbalance.

The corresponding values of the volumes of thorium and actinium emanations in equilibrium, with their parents, may be calculated from the half-value periods. They are extremely small.

In a mineral or a (solid) preparation of radium the emanation is occluded and very little of it escapes. By heating the mineral or preparation strongly, varying fractions of the total may be obtained, but the greater part of the gas may be driven out by heating to about 800° . The radium emanation may be pumped out directly, but it is usually necessary to wash it out with another gas, *e.g.* oxygen, as the amount is very small.

When an aqueous solution of a radium salt is kept in a closed flask, the emanation is evolved, together with oxygen and hydrogen produced by the decomposition of the water. The hydrogen produced is about 5% to 10% in excess of that equivalent to the oxygen present, due, possibly, to the action of the

radiations on the water resulting in the production of hydrogen and hydrogen peroxide. To obtain the emanation from this the gas is carefully pumped off and then exploded. All the oxygen and most of the hydrogen are converted into water. The residual gas is then led into a glass U-tube or a spiral cooled in liquid air. The emanation condenses at low pressures at about -150° , so that it is at once condensed in the U-tube or spiral, and the residual hydrogen pumped off. The emanation usually contains at this stage some carbon dioxide produced by the oxidation of organic matter; this is removed by leaving the gases in contact with solid KOH in a tube of the apparatus.

In the laboratory the gases over a radium salt are initially kept at a very low pressure so that subsequent purification may be rendered easier. As the half-value period of the emanation is 3.85 days, a solution of radium initially freed from its emanation will reform half its equilibrium amount in 3.85 days, three-quarters in 7.70 days, seven-eighths in 11.55 days, and so on. If the accumulated emanation be pumped off once a week, nearly three-quarters of the maximum amount of emanation available can be removed, purified, sealed up, and used for experimental work. This is a common procedure in laboratories. The valuable radium preparation is not itself handled for experiments. It merely generates under conditions of safety the emanation which, with its successive disintegration products, is as valuable for most experimental work as the radium preparation itself. If the tube of emanation be broken or lost there is a loss of time (in waiting for more to accumulate in the radium solution)

but not of money. On the other hand, the emanation decays to half-value in 3.85 days, so that the tubes lack permanence. In many cases, however, this is not found to matter.

In estimating radium by the ionisation due to the emanation, a simpler procedure suffices. The radium solution is heated, and the gases driven into a gas-holder by bubbling air slowly through the solution. In this way the emanation may be completely expelled. (See also p. 95.)

Radium emanation was called Niton ("the shining one") by Ramsay, so that this name would harmonise with those of the other inert gases. Niton has also been proposed as a common name for the three emanations. The new name has found its way into textbooks of chemistry, but it is doubtful if any improvement on such a descriptive name as emanation is necessary.

84 POLONIUM OR RADIUM F Po (210): Group VIA

(a) *Discovery*.—Polonium was discovered by M. and Mme Curie in pitchblende, from which it was separated with the bismuth of the mineral. The name was given in honour of the country in which Mme Curie was born.

(b) *Occurrence*.—Polonium may be separated from any uranium mineral or its residues, or from a preparation of radio-lead (radium D). In the laboratory, preparations of polonium may be obtained either from an old radium preparation (*i.e.* one which has been sealed up for years so that the emanation has not

escaped, and consequently the long-lived product of the emanation, radium D, and its successive products, have formed to an appreciable extent), or from the inside of a tube in which large quantities of emanation have been allowed to decay for some time. In both these sources the polonium has been generated as the penultimate disintegration product of radium or its emanation.

Polonium does not exist in weighable amount owing to its short half-value period of 136 days as compared with that of uranium, 5×10^9 years. Thus if 50,000 kilograms of a mineral containing 60% of uranium calculated as element were worked up, the maximum amount of polonium obtainable would be only

$$\frac{50,000 \times 1,000 \times 0.6 \times 136}{5 \times 10^9 \times 365}, \text{ i.e. } 0.0022 \text{ gram,}$$

or approximately, to 3 tons of uranium there corresponds 1 gram radium and 1.9×10^{-4} gram polonium. Experimental determination of its chemical properties in detail, its spectrum, and its atomic weight, is therefore possible only after its separation from very large quantities of carnotite or pitchblende.

(c) *Chemical properties*.—From its position in the periodic classification, Mendeleef predicted that polonium should be a homologue of tellurium and an easily-fusible, crystalline, non-volatile metal, grey in colour, and with a density of 9.3. Its atomic weight should be 212. It should form an oxide PoO_2 possessing both feeble acid and feeble basic properties. When further oxidised this oxide should become PoO_3 with properties similar to those of PbO_2 and Bi_2O_5 . The

metal should readily form alloys with the other metals.

It has not been possible, however, to test these predictions experimentally because of the extremely small amount of polonium that has yet been separated. The following results which have been obtained refer to polonium at a small concentration.

It resembles its homologue tellurium most closely in chemical properties. It behaves also like bismuth. When minerals are worked up for polonium, it is usual to separate it by precipitation with sulphuretted hydrogen in acid solution. It may be separated from bismuth by fractional precipitation of the basic nitrate with water, by fractional precipitation with sulphuretted hydrogen from solutions made very acidic with hydrochloric acid, and by sublimation in a vacuum.

Marckwald concentrated polonium from impurities in the following way. Stannous chloride was added to a solution in hydrochloric acid of polonium and impurities. Polonium and tellurium were precipitated. These bodies were next dissolved to form not too acid a solution, and the tellurium precipitated from it by the addition of hydrazine hydrate. The polonium remaining in solution can then be precipitated by stannous chloride.

It is usual, however, to separate polonium electrochemically by immersing a silver, a copper, a nickel, or a bismuth plate in a solution containing it. As much as 95% of the whole can be deposited on the plate. It is easy to choose conditions so that radium D and radium E, which are associated with polonium

(because they are its predecessors in the disintegration series, and because they too are precipitated from acid solution by sulphuretted hydrogen), are deposited in negligible amount only. In any case polonium can be freed from these bodies owing to the ease with which it is volatilised in air or hydrogen. (See also p. 157.)

CHAPTER IX

THE ANALYTICAL CHEMISTRY OF URANIUM

Minerals.—The principal minerals containing uranium are carnotite, pitchblende, autunite, bröggerite, cleveite, thorianite, and thorite. They have been briefly described in Chapter I.

Salts.—Uranium forms two classes of salts with acids, uranyl salts corresponding to the oxide UO_3 , and uranous corresponding to the oxide UO_2 . The former are the stabler and the better known. In uranyl salts only one of the atoms of oxygen in UO_3 is replaced by acid radicles, the divalent radicle UO_2 taking the place of a divalent metal.

Examples: UO_2Cl_2 ; $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$;
 $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$.

Uranyl salts are generally yellow in solution; uranous are green. Uranyl salts may be changed to uranous, and uranous to uranyl, by the methods used for converting ferric to ferrous salts and ferrous to ferric.

Uranium also forms two classes of salts with the strong bases, the uranates and diuranates corresponding to the chromates and dichromates. The formulæ of these are R_2UO_4 and $\text{R}_2\text{U}_2\text{O}_7$ respectively, R representing a monovalent metal.

The principal salts of uranium met with in radio-activity and in analytical work are the oxides, the nitrate, the acetate, the ferrocyanide, and the diuranates. These will now be briefly described.

Uranous oxide, UO_2 .—A brown powder formed by heating U_3O_8 in hydrogen.

Uranic oxide, UO_3 .—A chamois-yellow powder obtained by heating uranyl nitrate to 250° in a glass tube so long as acid fumes are given off. It is oxidised when strongly heated in air to U_3O_8 ; it is reduced by hydrogen to UO_2 .

Urano-uranic oxide, U_3O_8 .—The principal oxide. It is a dark green, almost black, powder obtained by igniting in air any oxide, uranyl nitrate, the carbonate or ammonium diuranate. It is soluble in concentrated nitric acid and in concentrated sulphuric acid. It is the form in which uranium is usually weighed when estimated gravimetrically. A thin film of it is used in radio-activity as a standard for α -particle measurements.

Uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.—This is formed as lemon-yellow rhombic crystals showing fluorescence, when an oxide is dissolved in nitric acid. It is very soluble in water, and soluble in alcohol, ether, and other organic solvents. It forms double salts readily with alkali nitrates. It is the commonest salt of uranium.

Uranyl acetate, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$.—This crystallises in yellow, monoclinic needles. It is used in photography and in the volumetric estimation of phosphates. It is a good salt to use in estimating uranium electrolytically.

Uranyl ferrocyanide, $(\text{UO}_2)_3\text{K}_2(\text{FeC}_6\text{N}_6)_2$.—Formed

when a solution of potassium ferrocyanide is added to a solution of a uranyl salt. It usually forms in the colloidal state (particles are negatively charged). It is converted into the diuranate by digestion with caustic alkalis or ammonia.

Ammonium diuranate, $(\text{NH}_4)_2\text{U}_2\text{O}_7$.—A yellow precipitate formed by adding ammonia to a solution of a uranyl salt (sometimes in the colloidal form). It is soluble in ammonium carbonate and in mineral acids; insoluble in ammonia and caustic alkalis. Ignition in air converts it quantitatively into U_3O_8 .

Potassium diuranate, $\text{K}_2\text{U}_2\text{O}_7$, and *sodium diuranate*, $\text{Na}_2\text{U}_2\text{O}_7$.—Yellow to orange precipitates formed when caustic potash or soda solution is added to the solution of a uranyl salt. They are soluble in mineral acids.

Peruranates.—Very unstable peruranates, obtained by the interaction of hydrogen peroxide and uranyl salts, are yellow in alkaline solution, and are occasionally utilised for the detection and colorimetric estimation of uranium.

Principal reactions.—Uranyl compounds in solution are not precipitated by hydrochloric acid, or by sulphuretted hydrogen in acid solution. Uranium is precipitated quantitatively by excess of ammonia in presence of ammonium chloride as ammonium diuranate, by caustic potash solution as potassium diuranate, and by caustic soda solution as sodium diuranate. These precipitates are all insoluble in excess of the precipitants. It is precipitated by ammonium sulphide in excess as uranyl sulphide, UO_2S . Sodium carbonate, potassium carbonate, and

ammonium carbonate precipitate uranium from uranyl salts, but in all three cases the precipitates are soluble in excess of the reagent, forming soluble double carbonates. The addition of caustic soda or caustic potash solution to these solutions causes precipitation. Neither ammonia nor ammonium sulphide, however, in like circumstances causes any precipitation. Uranium is precipitated quantitatively as uranyl ferrocyanide by a solution of potassium ferrocyanide, and as uranyl phosphate by a solution of ammonium dihydrogen phosphate.

It is not precipitated by excess of ammonia and ammonium carbonate solution (as mentioned above); nor by oxalic acid from mineral acid solutions; nor by aqueous hydrofluoric acid from neutral or acid solutions. These are the principal reactions used in detecting uranium, in separating it from other metals, and in estimating it gravimetrically.

Separations.—From the metals of the first and second groups by saturating a solution of the metals containing not more than 1 c.c. of concentrated hydrochloric acid per 50 c.c. of solution with excess of sulphuretted hydrogen in the cold.

From the metals which are precipitated by ammonia in presence of ammonium chloride the separation depends upon the solubility of ammonium diuranate in an excess of a strong solution of an alkali carbonate in the cold.

Iron is the commonest of these, and it may be separated from uranium by two other methods: (1) By adding ammonia, ammonium carbonate, and ammonium sulphide, which precipitates the iron completely and

retains the uranium in solution; or (2) by the ether method, which, although not so quick, is more complete, and is usually preferred. The ether method is carried out as follows: the mass containing the uranium and the iron is converted into chlorides by evaporating it to dryness twice with 10 c.c. of HCl (density 1.20). The dry mass is then taken up with 10 c.c. dilute HCl (1.10), and heated till the salts are dissolved, but not long enough to lose any of the acid by volatilisation. The cool solution and rinsings are made up to 25 c.c. and poured into a 250 c.c. separation funnel. 75 c.c. of ether free from alcohol and previously shaken up with HCl (1.10) are added, and the whole shaken for ten minutes, the pressure being relieved occasionally.

After shaking, the two solutions are allowed to separate, and the lower aqueous HCl solution of uranyl chloride with some iron drawn off into another separation funnel. The ether solution of ferric chloride is twice washed with 10 c.c. dilute HCl (1.10), and the washings, after separation from the iron solution, are run into the funnel containing the uranium.

To this 50 c.c. ether are added, and the whole process repeated, and again with 30 c.c. ether, so that altogether three extractions are made. The final aqueous solution of uranyl chloride is free from iron, and none of the uranium goes with the iron into the ether. It is important that the solution of HCl have a density of 1.10. Any ether in the aqueous solution is allowed to evaporate spontaneously by exposure before the uranium is estimated by any of the standard methods.

To separate uranium from all other metals, the following procedure works satisfactorily. Remove the

H_2S group in the usual way. Remove thorium and the rare earths, if present, by precipitating them with aqueous hydrofluoric acid from mineral acid solution; filter and expel the hydrofluoric acid by boiling. Next precipitate with ammonia, filter, dissolve the precipitate in acid; repeat this procedure twice. The solution obtained is completely free from those metals which are not precipitated by ammonia and ammonium chloride. To this solution, if ammonia and excess of a strong solution of an alkali carbonate in the cold be added, uranium alone remains in solution.

Uranium may be separated easily from the alkali and alkaline earth metals and zinc, but not from iron, cobalt, and nickel by electrolysis.

The conditions are for 0.1 gram U_3O_8 :

- (a) Dilution of solution, 125 c.c.
- (b) Temperature, 70°C . Time, 6 hours.
- (c) Solution to contain 0.1 c.c. of 30% free acetic acid.
- (d) Current of 0.04 ampères for 100 sq. cm. of cathode surface.

Uranium alone is precipitated as $\text{U}_3\text{O}_8 \cdot 3\text{H}_2\text{O}$, which on ignition becomes U_3O_8 .

From minerals containing phosphates (autunite, for example), uranium is separated from the filtrate from the sulphuretted hydrogen group by precipitation with potassium ferrocyanide. The colloidal solution becomes coagulated by adding a strong solution of salt or of aluminium chloride. The precipitate of uranium ferrocyanide is filtered off, and decomposed by caustic potash solution into potassium diuranate, which is dissolved in acid, and ammonium diuranate precipi-

tated from the solution by ammonia, and ignited to form U_3O_8 .

Atomic weight of uranium.—Hönigschmid made recently an accurate determination of the ratio $\text{UBr}_4 : \text{AgBr}$, and found a mean value of 238.15.

Estimation of uranium.

$$0.848 \text{ U} = \text{U}_3\text{O}_8$$

$$\text{U} = 1.179 \text{ U}_3\text{O}_8.$$

Gravimetric.—Uranium is precipitated as ammonium diuranate by NH_4OH in presence of NH_4Cl , and the precipitate ignited in air or oxygen to U_3O_8 . The conversion of the precipitate into UO_2 by igniting in hydrogen gives slightly inaccurate results, and is less convenient. The precipitation of uranium as phosphate and estimation as pyrophosphate $(\text{UO}_2)_2 \text{P}_2\text{O}_7$, which is often given in textbooks, is tedious and inaccurate, and is not recommended. Electrolytically it is separated as hydrated U_3O_8 from warm solutions of uranium acetate, uranyl nitrate, or uranyl sulphate, and converted by ignition into U_3O_8 . The following particulars regarding this operation are given by Smith (*Electro-Analysis*, 6th ed., p. 158):

Salt taken.	U_3O_8 present in grams.	Dilu- tion, c.c.	Current.	Volts.	Tem- perature.	Time, hours.	U_3O_8 found in grams.
Acetate	0.0986	125	N.D. ₁₀₇ = .3 A.	12.2	70°	5	0.0989
„	0.2298	125	N.D. ₁₀₇ = .07 A.	4.25	70°	5½	0.2299
Nitrate	0.1222	125	N.D. ₁₀₇ = .035 A.	4.6	70°	5½	0.1225
Sulphate	0.1320	125	N.D. ₁₀₇ = .02 A.	2	75°	6½	0.1320
„	0.1393	125	N.D. ₁₀₇ = .04 A.	2.25	75°	5	0.1395

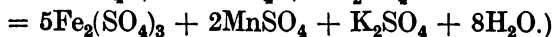
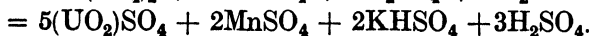
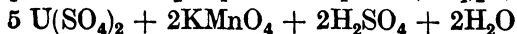
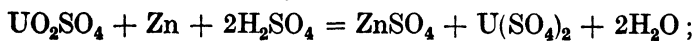
To the uranium acetate solutions was added 0.2 c.c. of 29% acetic acid.

For the rapid precipitation with the use of a rotating anode (600 revolutions per minute) the following particulars are given by Smith :

Salt taken.	U ₃ O ₈ present in grams.	Acetic acid, c.c.	Sodium acetate in grams.	Current in amperes.	Volts.	Time in minutes.	Temperature.	U ₃ O ₈ found in gram.
Uranyl sulphate	·1527	0·2	2½	3	14	18	room	0·1513
„	·2613	0·25	5½	7	15	8	60°	0·2611
„	·2613	0·25	4½	4	12	30	50°	0·2611

The dilution in all cases was 125 c.c.

Volumetric.—In absence of, or after separation from, iron, uranium may be accurately and conveniently estimated volumetrically. It is reduced in sulphuric acid solution from the uranyl to the uranous state by excess of zinc, magnesium, or aluminium, or by amalgams of zinc or cadmium, and the filtered solution quickly oxidised by $\frac{N}{10}$ KMnO₄ solution.



It is seen that 5U(SO₄)₂ is equivalent to 10FeSO₄

i.e. 1U = 2Fe.

1 c.c. of the $\frac{N}{10}$ KMnO₄ solution is consequently equivalent to 0·01191 gram U.

The solution of uranyl sulphate containing from 2% to 5% by volume of H₂SO₄ is poured into a flask

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containing 50 grams of pure amalgamated zinc 20 to 30 mesh, and the mixture is heated till a dark brown colour is developed. The flask is then cooled very rapidly under the tap, and the solution filtered from the zinc by pouring it through a small pulp filter. The zinc is washed with cold water by decantation, and air is aspirated through the filtrate and washings for a minute, and the clear green solution is then titrated with $\frac{N}{10}$ or $\frac{N}{20}$ KMnO_4 . Recently it has been found that one minute's shaking with a liquid amalgam of cadmium or zinc is sufficient to reduce the solution quantitatively to the uranous condition.

To ascertain the state of oxidation of the uranium in the mineral, the method usually used is that of Hillebrand. Two grams of the finely powdered mineral are introduced into a stout glass tube together with 20 to 30 c.c. dilute H_2SO_4 (1 part of acid to 5 of water). The air is then displaced with CO_2 , and the tube sealed off and heated at 180° for several hours till decomposition is complete. The solution obtained is diluted with recently boiled water, and the uranous sulphate titrated with $\frac{N}{10}$ KMnO_4 solution as in the experiment described above.

Special tests.—(1) To a solution of a uranyl salt add hydrogen peroxide or sodium peroxide and potassium or sodium carbonate. A cherry-red colour is produced, which in dilute solution becomes intensely yellow. A tenth of a milligram can be detected in this way. Iron should not be present.

(2) The precipitate resulting from the action of

potassium ferrocyanide upon uranyl salts varies in colour from blood-red to the colour of cocoa. It resembles that formed with cupric salts, but may be distinguished by its decomposition on treatment with caustic potash, with the formation of yellow insoluble potassium uranate.

Estimation of uranium in carnotite.—About 10 grams of the finely powdered mineral is heated with concentrated HCl till nothing further dissolves, and the whole filtered. The filtrate is diluted and H_2S passed through it till precipitation is complete, and then filtered. The filtrate is then evaporated to dryness, and a little HNO_3 added to oxidise the vanadium to vanadic acid, and NaOH added in excess. The filtrate contains sodium vanadate and sodium hydroxide, and the precipitate the uranium. The precipitate is treated with a hot saturated solution of ammonium carbonate, boiled thoroughly, and filtered. The filtrate is acidified with HCl and boiled till all CO_2 has been expelled. NH_4OH is added in excess and the precipitate treated as described on p. 119, the uranium being weighed as U_3O_8 .

Uranium in carnotite by Frichte's method.—Half a gram of finely powdered ore is heated for half an hour with 20 c.c. nitric acid in a 200 c.c. flask; 10 c.c. of water are then added, the solution neutralised with a saturated solution of sodium carbonate, a further quantity of 5 c.c. of sodium carbonate solution and 20 c.c. of a 20% sodium hydroxide solution added, and the solution boiled for half an hour. In presence of sodium hydroxide, sodium carbonate precipitates the uranium, vanadium, and iron, but the vanadium pentoxide

dissolves again in the sodium hydroxide solution. The precipitate is filtered off and washed with dilute sodium hydroxide solution until the filtrate gives no vanadium reaction. The residue is dissolved in 20 c.c. dilute nitric acid (1 : 1), diluted with 40 c.c. water, neutralised with ammonia, 40 c.c. saturated ammonium carbonate solution added, and the solution heated, but not boiled. Ferric hydroxide is precipitated, and the uranium remains in solution. The precipitate is filtered off, washed thoroughly with 2% ammonium carbonate solution, and an excess of dilute sulphuric acid added to the filtrate, which is then evaporated until sulphuric acid fumes begin to evolve. It is then reduced with zinc, and re-oxidised with permanganate as described in volumetric analysis.

Determination of uranium in pitchblende.—About 1.5 grams of well-ground ore are decomposed in a beaker covered by a clock glass by 10 c.c. HNO_3 (1.42) and 5 c.c. water, the whole heated on a water-bath, and evaporated to dryness. After cooling the mass is treated with 50 c.c. water and 3 c.c. nitric acid, and the solution boiled. Silica is filtered off, washed with boiling water, dried, and weighed if necessary. As lead is usually the only "Group Two" body present, it may be removed by evaporating the solution with sulphuric acid till fumes of SO_3 are given off, diluting, and filtering off the lead sulphate. If it is not, the filtrate from the silica is diluted to 200 c.c. and H_2S passed through the cold solution for an hour. The precipitate is filtered and washed with H_2S . The filtrate and washings from the sulphides are at first slowly heated and finally boiled in order to expel

H_2S gas. A few drops of nitric acid are then added to oxidise the iron. If thorium and rare earths are present in the mineral, transfer solution to a platinum dish, add excess of aqueous HF , filter off thorium and the rare earths which are precipitated quantitatively (it is necessary to use platinum vessels and filter-funnel or glass apparatus coated with paraffin wax), and boil off excess of HF . To this solution ammonia in excess and 150 c.c. of a saturated solution of ammonium carbonate are added and the whole thoroughly boiled. The precipitate of ferric hydroxide is filtered off and washed first by decantation, and later on the filter with hot water. The filtrate and washings containing the uranium are evaporated to half-volume, slowly neutralised with HCl (1.20), and about 3 c.c. of excess added. The whole is then boiled for half an hour till all the carbon dioxide is expelled. A solution of ammonia (0.90), free from carbonate, is then added in excess, and the whole boiled for fifteen minutes. The voluminous amorphous precipitate of yellow ammonium uranate is thus converted into a more crystalline form, darker in colour, which is easily washed. The precipitate is washed three times by decantation, and twice on the filter, with a hot dilute solution of ammonium nitrate. This prevents the precipitate from becoming colloidal and running through the filter, as it tends to do when washed with hot water only. The precipitate may be dried or not, and then placed in a platinum crucible, heated first cautiously and gently, then ignited in the blowpipe flame for ten minutes, the crucible being kept in a slanting position to allow air to circulate freely in the

crucible. A stream of oxygen is not necessary. The crucible is finally cooled in a decreasing bunsen-flame, then in the desiccator, and weighed.

Estimation of uranium in autunite by the method of Fresenius and Hintz.—About 0.5 to 1 gram of the mineral is dissolved in hydrochloric or nitric acid, and the silica separated from the solution by filtration in the usual way. Excess of a solution of potassium ferrocyanide is added to the solution, and the colloidal uranium ferrocyanide resulting coagulated by saturating the solution with sodium chloride. When the precipitate has settled, in an hour or two, it is first washed by decantation, and then on the filter-paper with water containing sodium chloride. The precipitate is then treated on the filter with dilute potassium hydroxide solution in the cold, by closing up the end, and leaving the solution in contact with it for ten minutes. This operation converts the uranium ferrocyanide into potassium diuranate. When this is completed, as shown by the change of colour from chocolate to yellow, the precipitate is washed uninterruptedly with water containing ammonium chloride and ammonia until the filtrate, on acidifying, shows no traces of potassium ferrocyanide.

The potassium diuranate is then carefully dissolved off the filter with hot dilute hydrochloric acid; ammonia is added to the solution, and the ammonium diuranate filtered off in the usual manner, ignited, and weighed as U_3O_8 .

CHAPTER X

THE ANALYTICAL CHEMISTRY OF THORIUM

Minerals.—The principal thorium minerals have already been described in Chapter I. They are monazite sand, thorite, orangite, and thorianite.

Salts.—Thorium is not a powerful metal, but its base-producing properties are much more evident than its acid-producing. In its compounds it is always quadrivalent. The principal salts met with in radio-activity and in analytical work are the oxide, the hydroxide, the nitrate, the sulphate, the fluoride, and the oxalate. These will now be briefly described.

Thorium oxide, thoria, ThO_2 .—A dense white powder insoluble in acids, the more so the more strongly it has been ignited. It may be obtained by ignition of the hydroxide, the nitrate, the carbonate, the hydrated fluoride, the oxalate, and certain organic salts of thorium. It is most easily obtained in solution by fusing it with four times its volume of potassium bisulphate, dissolving the mass in water, precipitating the hydroxide by ammonia, and dissolving this in an acid.

Pure thoria does not glow brightly when heated, nor does it phosphoresce appreciably under the influence of cathode rays. It glows very brightly

when it contains small quantities of impurities, *e.g.* with 1% or 2% of cerium oxide as in the incandescent, gas-mantle.

Thorium hydroxide, $\text{Th}(\text{OH})_4$.—A heavy precipitate, readily soluble in mineral acids and alkaline carbonates, insoluble in alkali hydroxides, obtained by adding solutions of ammonia or of caustic alkalis to a thorium solution. Barium carbonate solution in the cold, and sodium thiosulphate when boiling, also precipitate the hydroxide.

Thorium nitrate, $\text{Th}(\text{NO}_3)_4$.—Exists hydrated with 12, 6, and 5 molecules of water according to the conditions of crystallisation. The most usual compound of thorium is the purified commercial thorium nitrate, which is not a definite hydrate, but approximates in composition to $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, contains 1% or 2% of thorium sulphate, and on ignition gives 48% to 50% of thoria. It is very soluble in water.

Thorium sulphate, $\text{Th}(\text{SO}_4)_2$.—Is obtained anhydrous by treating thoria with concentrated sulphuric acid, and heating till excess of acid has been evaporated, or by heating the octahydrate to 400° . It is soluble in four times its weight of ice-cold water; the solution being supersaturated at all temperatures from 0° to 100° . Between 0° and 43° the octahydrate is deposited, above 43° the tetrahydrate. Compounds with 2, 6, and 9 molecules of water also exist. The octahydrate is the most important, since it is this salt which is used to purify thorium preparations by fractional crystallisation technically.

Thorium fluoride, $\text{ThF}_4 \cdot 4\text{H}_2\text{O}$.—Is a gelatinous precipitate, obtained on adding hydrofluoric acid to

thorium salts, which changes on standing to a white powder. It is insoluble in excess of the precipitant. This serves to separate thorium from zirconium. Ignition converts the fluoride into the oxide.

Thorium oxalate, $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$.—Is precipitated completely by adding oxalic acid to a thorium salt in excess, even in the presence of a considerable quantity of a mineral acid. It is soluble in ammonium oxalate. It is crystalline or amorphous according to conditions. A characteristic property is its power of forming complex salts with alkali oxalates. It is obtained in solution most easily either by ignition, followed by fusion with KHSO_4 , precipitation of the thorium by ammonia from a solution of the melt, and finally dissolving the hydroxide in mineral acid; or, by boiling the oxalate with stick caustic potash, thereby converting it into hydroxide, and dissolving the hydroxide after filtration in mineral acid.

Principal reactions.—Thorium compounds in solution are not precipitated by hydrochloric acid, or by sulphuretted hydrogen in acid solution. Thorium is precipitated quantitatively by :

- (a) Ammonia and ammonium chloride as hydroxide.
- (b) Caustic alkalies in solution as hydroxide.
- (c) Oxalic acid from mineral acid solution as oxalate.
- (d) Aqueous hydrofluoric acid from mineral acid solution as hydrated fluoride.
- (e) Hydrogen peroxide from neutral or slightly acid solution as peroxide.
- (f) Sodium thiosulphate from neutral or slightly acid solution of chlorides as hydroxide.
- (g) *m*-nitrobenzoic acid from neutral solution as the

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m-nitrobenzoate, and by many weak organic acids and bases.

It is precipitated as oxalate also by ammonium oxalate, but in excess of this reagent the oxalate is soluble.

Potassium, sodium, or ammonium carbonate precipitates thorium as carbonate, which, however, is soluble in excess of the reagent.

Thorium compounds resemble those of cerium in the ceric condition. Thorium resembles the rare earths in being precipitated by hydrofluoric acid and by oxalic acid. Like cerium, its double sulphate with potassium is insoluble in excess of potassium sulphate.

Thorium salts are colourless except when the colour is due to the acid with which it is combined.

These reactions are the principal ones used in detecting thorium, in separating it from other metals and in estimating it.

Separations.—From the metals of the first and second groups as with uranium.

From uranium and the common metals of the ammonia and ammonium chloride analytical group by precipitating thorium with excess of aqueous hydrofluoric acid as fluoride.

From cerium and the rare earths (which are precipitated along with thorium by the above reagent) by converting the fluorides by ignition into oxides, bringing the oxides into solution by fusion with bisulphate, etc., and precipitating the thorium from a neutral solution of the nitrates by *m*-nitrobenzoic acid. The thorium thus precipitated as nitrobenzoate may contain traces of cerium, etc. It is obtained in solution

and a second precipitation made with *m*-nitrobenzoic acid from a neutral solution of the nitrates. The ignited precipitate is pure thorium oxide.

Thorium may also be separated from various bodies in the following way :

From zirconium by the fact that the oxalate of zirconium is soluble in excess of oxalic acid ; from cerium and yttrium by the fact that, while ammonium oxalate precipitates all three as oxalates, that of thorium alone is soluble in excess, and is not precipitated by diluting the solution. From cerium, lanthanum, the didymiums, and yttrium by precipitation of thorium by sodium thiosulphate.

The best reactions, and, with valuable material such as isotopes of thorium like ionium, the safest reactions are the precipitation of thorium or its isotopes as hydroxide (with ammonia), as oxalate, as hydrated fluoride, and as nitrobenzoate.

Atomic weight.—The atomic weight of thorium is 232.15, based on a series of analyses of thorium bromide. Two values were obtained, namely, 232.152 from the silver ratio, and 232.150 from the Ag : Br ratio, when Br = 79.916 (Hönigschmid and Horowitz).

Estimation of thorium.—Thorium is always estimated gravimetrically as ThO_2 obtained by the ignition of the hydroxide, the peroxide, the oxalate, the fluoride, or the nitrobenzoate.

Estimation of thorium in thorianite, according to the method of Dunstan and Blake.—Two grams of the finely powdered mineral were dissolved in 15 c.c. HNO_3 (density 1.4), and after decomposition was

complete the solution was diluted and filtered. The insoluble residues contain silica, zirconia, etc. The ZrO_2 is extracted by fusion with KHSO_4 , and the residue is then treated with HF to estimate silicon in the usual way. The filtrate from the insoluble residue was diluted to 300 c.c. and 5 c.c. HCl added. H_2S was passed into the liquid to precipitate the lead, which was later converted into sulphate and weighed. The filtrate was boiled to remove H_2S , and the last traces of this substance were oxidised by bromine water. To the hot acid solution, amounting to about 350 c.c., ammonium oxalate was added in excess, but not till alkaline, and the precipitate of the oxalates of thorium, cerium, etc., was allowed to settle overnight and then it was filtered. The filtrate was evaporated to dryness, treated with HNO_3 to destroy oxalic acid, and diluted with water. From this solution calcium and magnesium were separated from the other metals by precipitating the latter with NH_4OH and NH_4Cl . This precipitate was dissolved in HCl , the excess of acid neutralised, and the solution diluted to 500 c.c. A few drops of HNO_3 were added to oxidise the iron. The liquid was neutralised with a few drops of ammonia, and excess of ammonium carbonate solution added, and then ammonium sulphide. In these circumstances the iron is precipitated as sulphide, and the uranium remains in solution. The filtrate from the iron was acidified with HCl , boiled to remove all the carbon dioxide, and the uranium in solution was precipitated with ammonia and weighed finally as U_3O_8 .

The precipitate of thorium, cerium, and other oxalates is dried, and the oxalate decomposed by nitric acid,

The solution is evaporated to dryness till all free nitric acid has been removed, and thorium separated from cerium and other bodies by two precipitations with meta-nitrobenzoic acid as described in the analysis of monazite sand above. Or thorium may be separated by three precipitations with sodium thiosulphate solution. The solution of nitrates is diluted to 250 c.c., made slightly acid, and boiled. Sodium thiosulphate is added till no further precipitate of thorium is obtained. The liquid is boiled for a short time, the precipitate is filtered off and dissolved in hydrochloric acid, and the operation twice repeated to separate the cerium completely. In both cases the thorium is ignited and weighed as ThO_2 .

Estimation of thorium in monazite sand by Neish's method.—Two grams of the sand were ground to a fine powder and weighed out into a porcelain crucible, about 10 to 15 c.c. of concentrated sulphuric acid added and stirred with a small glass rod, which is left in the crucible throughout the digestion. The crucible was left on a hot plate, heated gradually and stirred cautiously to allow the escape of bubbles of gas, which are only formed at first, and cause loss if the heating is not done carefully. The heat was increased until a constant cloud of sulphur trioxide was given off. When the excess of acid had evaporated, more acid was added, the crucible cooled, the contents were stirred with the glass rod, and the digestion continued. Digestion should be for three hours, or more if time is available, but three hours is sufficient. At the end of the digestion the phosphates present in the monazite sand were

all changed to sulphates. The crucible now contained about 10 c.c.. This was well stirred, and after cooling the crucible in ice water the mass was allowed to drop from the rod, a drop at a time, with constant stirring, into a beaker containing 600 c.c. of water cooled to 0° C.

After all the liquid was added the crucible itself was placed in the beaker, and the whole allowed to stand, best overnight. If it is a refined sand and free from quartz, the residue on the bottom of the beaker should be small, but if there is a flocculent precipitate, it is apt to be hydrated sulphate of thorium. In this case the best thing to do is to start afresh, using greater care in adding the mass to the ice water, and to have enough free acid present to make the mass liquid enough, so that when a drop of it is added to the beaker it soon dissolves, leaving a fine white powder instead of sinking to the bottom as a hard lump, which it will do if too little acid is present.

The solution was filtered into a larger beaker and heated to boiling. A boiling solution of oxalic acid saturated in the cold was added gradually to the solution, with constant stirring, a large excess being used in order to make the precipitation complete in presence of so much sulphuric acid, and also to take any zirconium into solution which would otherwise be precipitated later by the sodium thiosulphate. An excess has no solvent effect on the thorium whatever. The solution was allowed to stand, and when cool the white crystalline precipitate of oxalates of thorium, cerium, lanthanum, and didymium was filtered and washed with a dilute solution of oxalic acid. The precipitate

should stand many hours, better, if possible, overnight. The precipitate and paper were transferred to the precipitation beaker, 10 to 15 grams of stick caustic added, 25 to 50 c.c. of water, and the whole heated to boiling, washing down any oxalates that were attached to the sides of the beaker. The oxalates were changed to hydroxides having a silky appearance and yellow owing to the oxidation of cerium. The solution was diluted to about 300 c.c., filtered, and washed with water till free from alkali. The hydroxides were dissolved into the precipitation beaker with hot dilute nitric acid (1 to 5). This solution of the nitrates was evaporated to dryness on the water-bath, moistened with water, and evaporated till every trace of free nitric acid was driven off.

The nitrates were dissolved in 500 c.c. of water, and 150 to 250 c.c. of meta-nitrobenzoic acid solution slowly added, with constant stirring. The whole was heated on the water-bath at 60° to 80° till the precipitate had all collected and settled to the bottom. It was then filtered, washed by decantation, using a 5% solution of the precipitant, then placed on the filter and washed with the same filter solution. The precipitate was dissolved by hot dilute nitric acid (1 in 5) into the precipitation beaker, the paper well washed, and diluted to 600 c.c. The thorium was then precipitated by KOH. This causes at first a reprecipitation of the flocculent meta-nitrobenzoate, but a slight excess changes it to hydroxide. The solution was then diluted and filtered through the same paper, the precipitate washed and dissolved by hot dilute nitric acid (1 to 5) into the same beaker, the solution evaporated to dryness,

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as before, the mass dissolved in 600 c.c. of water, and the solution precipitated with meta-nitrobenzoic acid. The moist precipitate is finally ignited, and the resulting thorium oxide weighed. It should be snow-white.

The estimation of thorium in thorite and orangite are obvious from the composition of these minerals, and need not be given here.

CHAPTER XI

THE SEPARATION OF THE RADIO-ELEMENTS INDIVIDUALLY

THE following are the principal primary and secondary sources of the radio-elements :

TABLE 12

- (1) Uranium minerals.
 - (2) Uranium residues.
 - (3) Salts of uranium.
 - (4) Salts of ionium.
 - (5) Salts of radium.
 - (6) Radium emanation.
 - (7) Active deposit of radium.
 - (8) Emanation tubes.
 - (9) Salts of radio-lead (RaD).
-
- (10) Salts of protactinium.
 - (11) Salts of actinium.
 - (12) Salts of radio-actinium.
 - (13) Salts of actinium X.
 - (14) Actinium emanation.
 - (15) Active deposit of actinium.
-
- (16) Thorium minerals.
 - (17) Thorium residues.

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- (18) Salts of thorium.
- (19) Salts of mesothorium.
- (20) Salts of radiothorium.
- (21) Salts of thorium X.
- (22) Thorium emanation.
- (23) Active deposit of thorium.

General.—The discovery of isotopes has led, as we have seen, to a great and interesting simplification of the chemistry of the radio-element, namely its reduction to the study of ten different elements only. In all chemical separation work with radio-elements the hypothesis of isotopes is accepted as true, *i.e.* it is assumed that :

(1) Isotopes have identical chemical properties.

(2) If the chemical properties of an element be known, the chemical properties of all its isotopes are known.

(3) If two isotopes are found together in nature, or in a preparation, or if they be mixed, it is not possible to separate them at all, or to effect a concentration of one of them in the mixture in the least degree.

The second and third assumptions are, of course, deductions from the first; they render it more explicit. (3) is a statement of the negative side. It implies, for example, that mesothorium 1 and radium, when mixed, cannot be separated, nor can ionium and thorium, nor can uranium I and uranium II; lead cannot be separated from RaB, RaD, Pb₃₀, AcB, AcD, ThB, or ThD.

These rules seem to be final, and with our knowledge in its present state, it would appear that any time

spent in attempting to devise a *chemical* separation of two isotopes is wasted.

It is usually a matter of difficulty to choose one's minerals or preparation so that the radio-element separated from them is free from isotopes. For example, uranium I and uranium II can never be separated since both bodies have long half-value periods; the possibility of the latter decaying away in time and leaving the former free from it is therefore excluded.

• The preparation of radium free from mesothorium 1, on the other hand, is a simpler problem, since many uranium (and therefore radium) minerals contain thorium (and hence mesothorium 1) in negligible amount only; but it is not possible to obtain mesothorium 1 free from radium *from minerals*, since all thorium minerals happen to contain a percentage of uranium, and therefore of radium. Mesothorium 1 can, however, be obtained free from radium (but not from thorium X) by separating it from a purified preparation of thorium, in which in time it has accumulated. The thorium X, having a quick half-value period, soon decays away, leaving the mesothorium 1 free from isotopes. Many other examples might be quoted here, but it would be better to deal with the separation methods for individuals later.

The positive side of (1), (2), and (3), on the other hand, leads to the following proposition:

A radio-element can be separated from a preparation or a mineral by adding a small quantity of the type-element, and then proceeding as though the type-element alone were being separated.

Thus, RaB may be separated from RaC by adding

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to a solution of both small amounts of soluble salts of lead and bismuth; the lead is then separated from bismuth in the ordinary way, and carries with it (quantitatively) the RaB, whilst the bismuth fraction contains the whole of the RaC. ThB may be separated from ThC by this method, also AcB from AcD, RaD from RaE, and RaB from RaE. The separation of UX₁ from U by the addition of the former's type, thorium, has already been mentioned (p. 18).

Ionium is separated from pitchblende by adding thorium to a solution of the mineral, separating the thorium and purifying it. The ionium remains quantitatively with the thorium.

When the type-element itself is rare (U, Th, Pb, Bi, Tl are looked upon as "common," and Pa, Ac, Ra, and Po as "rare"), the next lower member of the group is used instead of the type-element to effect the separation; Ta for Pa, La for Ac, Ba for Ra, and Te for Po. These homologues resemble the type-elements sufficiently to allow of their isotopes being separated with them. Thus protactinium was separated from pitchblende residues by adding a soluble salt of tantalum, and separating the tantalum from the other elements by the ordinary methods. Similarly, any of the isotopes of radium may be separated from minerals or preparations by first adding a soluble barium salt to the solution and separating out the barium. Mesothorium 2 (an isotope of actinium) may be separated from mesothorium 1 (an isotope of radium) by adding soluble lanthanum and barium salts to their solution, and separating the lanthanum from the barium, *e.g.* by precipitating the former with pure ammonia gas.

The subject of chemical separations, however, is rendered more complex than might appear from (1), (2), and (3) above for three reasons :

(a) When radio-elements of short half-value period are being separated, the element of time must be considered. If it is not, the body may have decayed to zero before it is prepared for investigation. Special methods applicable to radio-elements have been devised to replace ordinary chemical methods of separation for these elements.

(b) The majority of the radio-elements exist in the preparations which are usually dealt with in very minute concentration only. Now a chemical reagent might precipitate a radio-element, leaving the others from which it is being separated in solution ; but the amount of material precipitated may be so minute that it cannot be filtered. Sometimes, therefore, a solution of a type-element or even of a common element is previously added to the solution, so that when it is precipitated along with the radio-element it acts as a nucleus for purposes of filtration. The radio-element, although free from other radio-elements, is then associated with a relatively large mass of inactive impurity, which absorbs part of its radiations, and in general is objectionable. Special methods which include electrochemical separations have been devised to effect a clean separation of bodies which exist in minute concentration only, without rendering them impure as described above.

(c) Special procedure is often necessary to obtain a radio-element free from its isotopes. As has been stated, no chemical method is available once two isotopes

have come together. Time, however, *may* effect a separation, since one of the two isotopes may have a short half-value period relative to the other, so ~~that~~ it vanishes in due course by disintegration, leaving the other free from it. The presence of isotopes may also be avoided by preparing a suitable radio-active preparation, free from all the isotopes under consideration, in which the isotope which alone is wanted is produced in time by disintegration.

Two special methods of separation will now be described, that by recoil, and the electrochemical method.

Separation of radio-elements by the method of recoil.—It is possible to separate several radio-elements conveniently, quickly, and in a form free from the contamination which arises when a minute precipitate is separated by chemical methods, by the method of recoil. If a mass m and velocity v is expelled from an atom of mass M , then it is to be expected, from the principle of the conservation of momentum, that the residual atom of mass $M - m$ would recoil with a velocity V , where $(M - m)V = mv$. As the momentum of the α -particle is much greater than that of the β -particle, the product of a body expelling an α -particle recoils with a greater velocity than the product of a body expelling a β -particle. In both cases, but obviously much more easily in that of the α -particle change, the recoil atom may escape from the layer of radio-active substance, and be deposited on a plate of metal suitably arranged to catch it. It has been found that the recoil atom carries a single *positive* charge, and consequently the best yield of recoil atoms

is obtained by placing a metal plate *negatively* charged, say to 100 or 200 volts, near a plate covered with ~~active~~ matter. By this method of recoil several radio-elements were discovered: actinium C'' and thorium C''. The complexity of radium C was also shown by the recoil method.

The following are the principal bodies which may be separated by recoil. Radium B from radium A, radium C from radium B, actinium X from radio-actinium, actinium C'' from the active deposit of actinium, and thorium C'' from that of thorium. The method may be employed generally. The advantages of the recoil method are that (a) it is quick, an important factor for bodies of short periods like ACC'' and ThC''; (b) the product is free from contamination by other radio-elements; and (c) the product is obtained in a convenient form, say on a metal plate or a wire, and free from the impurities, associated with a chemical separation, which absorb part of the radiations. A drawback is the poverty of the yield, which is not quantitative as it may be in purely chemical operations, since only half of the recoil atoms have an opportunity of being concentrated on the negatively-charged plate (the other half being absorbed in the plate on which the active material, producing the recoil atoms, is deposited).

Separation by electrochemical methods.—Electrochemical methods of separating radio-elements were used to some extent by the early workers. Thus, v. Lerch separated radium C from radium B, and thorium C from thorium B, simply by dipping a wire or a plate of nickel into a solution of both. Polonium was

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separated from radium D by immersing plates of bismuth in a solution. A detailed study of the separation of the radio-elements, embracing the results of previous workers, was made by v. Hevesy (1912).

He found that :

(a) It is not necessary, in carrying out a separation, to have two electrodes and an externally-applied voltage as in a separation of the common elements. Immersion of a single wire or a plate of a metal into a solution in suitable circumstances ensures the maximum possible deposition on it of the radio-element to be separated.

(b) *Every* radio-element is deposited in measurable quantity on *any* metal dipped into *any* solution of it. The quantity is often exceedingly minute, being undetectable by any methods but those of radio-activity. It varies in amount with the conditions, and is a function of the potential difference between the metal and the solution containing the radio-active substance.

(c) The following groups of radio-elements possess identical electrochemical properties.

Radium, Actinium X, Thorium X.

Radium B, Actinium B, Thorium B, Radium D.

Radium C, Actinium C, Thorium C, Radium E.

Actinium C'', Thorium C''.

(These are, of course, groups of isotopes, but v. Hevesy's observations were made before the hypothesis of isotopes was put forward.)

(d) Electrochemical methods are not practicable for separating the radio-elements which occur in the three disintegration series before the emanations except uranium X₂ and mesothorium 2. They are most

useful in separating (1) radium C from radium B ; (2) actinium C from actinium B ; (3) thorium C from thorium B ; (4) radium E from radium D ; and (5) polonium from radium D and radium E.

Practical methods of separating radio-elements electrochemically are based on two things :

- (1) Knowledge of the potential difference between metal and solution which causes the deposition of the radio-element it is desired to separate.
- (2) The fact that the addition of a type-element, which is inactive, to a solution containing a radio-active isotope hinders the deposition of that isotope.

(1) V. Hevesy's work was chiefly done with electrochemically definite systems and with the active deposits of the three emanations. He found there was a simple relation between the relative quantities of the B body and the C body deposited on a metal, and the difference of potential between the metal and the solution of one of its salts. The solution was prepared as follows : The active deposit was obtained by exposing a platinum wire to the emanation for a suitable time. When the A product had decayed and the B and C products were in equilibrium, they were dissolved off the wire by acid, the solution just neutralised, and added to a solution of an inorganic compound and made up to a known strength, usually normal or tenth-normal. The metal of the inorganic compound was then dipped into the solution for a definite period (say one minute), removed, washed, dried, and its α -particle activity determined in an electroscope. From measurements of change of this activity with time the relative quantities of the B and the C bodies could be calculated.

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This experiment was repeated with different metals—in each case the metal was dipped into a neutral solution of known strength of one of its own salts, and the relative amounts of B and C determined. The percentages of the B body or the C body of the total B and C deposited on the plate were plotted as ordinates, and, as abscissæ, the potential differences of metal and solution, determined against the standard

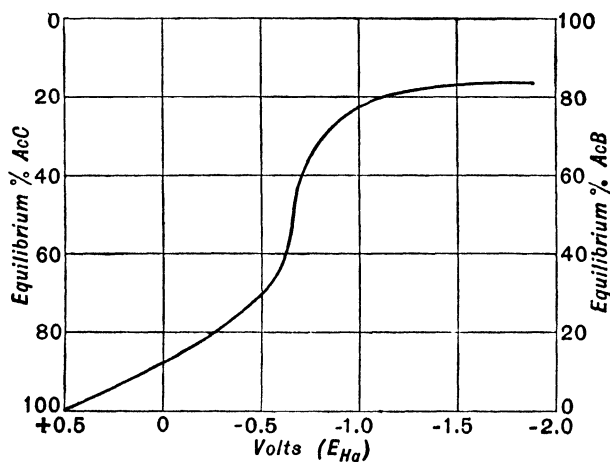


FIG. 11.

calomel electrode, necessary for producing this deposition. The curve shown in Fig. 11 was the result.

From the curve it is seen that if a silver plate be dipped in normal silver nitrate containing B and C in equilibrium, pure C is deposited on it, because in this case the potential drop at the surface of the metal is $E_{Hg} = +0.49$ volts. Silver dipped in decinormal silver nitrate solution brings out a little B with the C

because the potential drop at the surface of the metal is now $E_{\text{Hg}} = + 0.43$ volts. Cadmium dipped into semi-normal cadmium sulphate solution brings out 40% of the equilibrium amount of C and 60% of B, since the potential drop is $E_{\text{Hg}} = - 0.71$. If a plate of magnesium be dipped into a seminormal magnesium sulphate solution, B is deposited in great excess over C because the potential drop of the electrode is here, $E_{\text{Hg}} = - 1.9$ volt.

• V. Hevesy further showed that the potential difference between nickel and a hydrochloric acid solution of the active deposit is approximately that between silver and normal silver nitrate, and is different from the potential difference between nickel and a normal solution of a nickel salt ($E_{\text{Hg}} = - 0.53$). Nickel dipped into the hydrochloric acid solution is rendered passive and less electro-positive than in the second case, for it brings out pure C from the solution.

It is seen from the curve that it is not possible to obtain pure B, about 17% of the C body being deposited with 83% of B when the potential drop (that between Mg and $\frac{N}{2}$ MgSO_4) is $E_{\text{Hg}} = - 1.9$ volt.

(2) These results apply to the radio-elements mentioned when they are present in the extremely small concentrations in which they exist in the active deposits of the three series. But since lead is an isotope of RaB, AcB, ThB, and RaE, the concentration of any of these bodies can be enormously increased by adding to the solution of an active deposit a small quantity of lead salt. This leads to an important point in the separation of these radio-elements from others.

Suppose that a solution of RaB and RaC about to be electrolysed contains x atoms of the former, and that a plate when immersed in the solution has deposited upon it, in addition to the RaC, y atoms of RaB; if now a small quantity of a lead salt containing, say, 10^6x atoms of lead be added to the solution and the experiment repeated, lead will behave exactly like RaB, and the number of mixed lead and RaB atoms deposited will be about the same as before, *i.e.* y atoms; but as the ratio of inactive lead to active RaB is 10^6 to 1, the deposit on the plate will be almost free from RaB and so contain nearly pure RaC only. This is an illustration of the general principle mentioned in (2) on p. 139.

The addition of lead hinders the deposition of RaB, AcB, ThB, or RaD. Similarly, the addition of bismuth hinders that of RaC, AcC, ThC, or RaE; and the addition of thallium that of RaC'', AcC'', and ThC''. It will be realised, therefore, how important in electrochemical work is the presence of inactive type-elements as impurities in solutions to be electrolysed.

INDIVIDUAL METHODS OF SEPARATION

The general methods of separation described above, the list of preparations given in Table 13, and the information given in Tables 6, 7, and 8, provide sufficient knowledge to suggest suitable methods for obtaining any radio-element in as pure a state as possible. The methods employed in separating some of the individuals will now, however, be given, but the treatment makes no pretence to be exhaustive.

Uranium.—The separation of salts of uranium from minerals has been described already (p. 111).

U_I cannot be separated from its isotope U_{II}. Old preparations of uranium contain as impurities UX₁, UX₂, UY, UZ, and traces of Io and Ra. Uranium may be purified from these by adding to a solution of it a salt of barium and of a rare earth in solution, separating out the barium as sulphate (and with it the whole of the Ra and part of the rare earth, UX₁, UX₂, UY, UZ, and Io), and then the rare earth as fluoride (with it the remainder of the radio-active impurities). The test for purity is complete absence of β -particles. In one day after complete separation 2.8% of the equilibrium amount of UX₁ is formed. This may be removed at any time by adding to the solution a small quantity of a rare earth solution, and precipitating with aqueous HF, or a small quantity of erbium in solution and precipitating with meta-nitrobenzoic acid. In both cases UX₁ is quantitatively precipitated, the uranium remaining in solution.

Uranium salts are the convenient sources of UX₁, UX₂, UY, and UZ. A thin layer of the oxide U₃O₈ on a disc is used as a standard source of α -particle activity in electroscopic measurements. A thick layer of U₃O₈ in equilibrium, covered with a thin sheet of metal to keep out moisture and to absorb α -particles, is used as a standard source of β -particle activity in electroscopic measurements. It is prepared by igniting the nitrate or ammonium diuranate.

Uranium X₁.—UX₁ is best separated from salts of uranium in solution by adding a rare earth in solution and precipitating with aqueous hydrofluoric acid or with oxalic acid, or by adding a small quantity of erbium or thorium in solution and precipitating with

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m-nitrobenzoic acid. From large quantities of uranium nitrate it is usual to concentrate the uranium X_1 by fractional crystallisation, the uranium X_1 concentrating in the mother liquor. When sufficiently concentrated the uranium X_1 may be separated by the usual methods.

A preparation of UX_1 is a convenient one for demonstrating the exponential law of disintegration. It is the source of UX_2 and of UZ .

Uranium Y.— UY is a supposed product of uranium II and is an isotope of UX_1 . It is therefore separated from uranium salts along with UX_1 by the methods described for UX_1 . The half-value period of UY is about 25 hours, so that 25 hours after its complete separation from the uranium half of the equilibrium amount has been regenerated by it; in the same time less than 3% of the equilibrium amount of UX_1 has grown. This suggests a way of obtaining a preparation of UY with the minimum contamination of UX_1 .

Uranium X_2 .— UX_2 is separated from a concentrated solution of UX_1 by immersing a lead plate for a minute in it. Much of the UX_2 deposits on the lead plate, which is free from UX_1 . Or a soluble tantalum salt might be added to the solution of UX_1 and the Ta separated in the usual manner (see Uranium Z). With it goes UX_2 quantitatively. Its short period (1.15 minutes), however, favours the electrochemical method.

Uranium Z.—A new body, UZ , believed to be a branch product of uranium X_1 , was discovered by Hahn in 1921. It was isolated in the following manner. Uranium X_1 was enriched in the mother liquor from a

few fractional crystallisations of uranium nitrate from water. Uranium Z was found to be concentrated in the mother liquor also. To the latter was added ferric chloride solution, and the iron, carrying with it UX_1 and UZ, was precipitated by the addition of ammonia and ammonium carbonate. The iron precipitate is treated with a solution of tantalum in hydrofluoric acid, lanthanum nitrate is added, and the mixture is digested on the water-bath for some time with dilute hydrofluoric and sulphuric acids. The lanthanum and the uranium X_1 are thereby precipitated as insoluble fluorides, the former acting as a nucleus for the latter. The filtrate is evaporated, and the residue gently ignited, whereby the tantalum precipitate becomes insoluble in acid while the iron precipitate remains soluble. The latter is obtained in solution by concentrated hydrochloric acid, and the residue is warmed for some time with aqua regia and filtered after being diluted. The tantalum remains on the filter in a perfectly colourless condition. Uranium Z remains almost completely with the tantalum, only small quantities being found with the iron precipitate; both, however, retain small amounts of uranium X_1 , which can be almost completely eliminated by a second treatment of the iron tantalum solution with lanthanum nitrate. In this way Hahn found it possible to obtain specimens of uranium Z which are 99.5% radio-actively pure.

Ionium.—Io is prepared in quantity by separating and purifying thorium from large quantities of uranium minerals or residues. For experimental purposes it is usually separated from pitchblende, carnotite, or

autunite by adding to a solution of the mineral a solution containing about 20 milligrams of thorium and 20 milligrams of lanthanum, separating these out, and finally separating the thorium from the lanthanum by *m*-nitrobenzoic acid. The Io of the mineral goes quantitatively with the Th, and the Ac with the La.

Io prepared from uranium minerals not containing thorium has initially its isotopes UX₁, UY, and RdAc with it. These, having short half-value periods, decay away in time, and their products may be removed from the Io by reprecipitating the latter with *m*-nitrobenzoic acid. Large preparations of Io contain Th, for all uranium minerals seem to have traces of the latter, which, not noticeable in a quantitative analysis, amount to several milligrams or more when a large quantity of a source of Io is worked up. The effect of Th and its products in a large preparation of Io is usually very small, but, if it is desired, the products except the isotopes of ionium may be removed by the ordinary chemical methods.

Preparations of Io are used as standards of α -particle activity, when a more active standard than U₃O₈ is necessary. In them also the gradual growth of radium, according to the inverse exponential law, may be experimentally demonstrated.

Radium.—The separation has already been described (p. 91). Radium salts are used—

- (a) As source of radium emanation.
- (b) As source of RaD, RaE, and RaF.
- (c) As standard source of γ -ray activity in electroscopic measurements.
- (d) In medical work.

Radium may be temporarily freed from all its products in the following way :

(1) Add 10 milligrams of lead chloride to an HCl solution of the radium ; precipitate the lead completely with H_2S . The RaD, RaE, and RaF are precipitated quantitatively with the lead.

(2) Evaporate solution in a small evaporating dish on a water-bath to about 50 c.c., and keep it evaporating for six hours. Add cold water occasionally to keep the amount of solution constant. Add a little HCl if the radium tends to precipitate out. Every twenty minutes bubble air through the solution to remove any emanation not otherwise expelled. Six hours suffices for all the RaA, RaB, and RaC to decay to zero, and the expulsion of the emanation as it is formed by keeping the solution hot prevents their formation in solution. Finally, evaporate rapidly to dryness, first on the water-bath and later at 200° . This ensures radium temporarily freed from all its products.

Protactinium.—The separation of Pa from other radio-active substances in uranium minerals or residues has been described on p. 88. It is not yet possible to separate it from its homologue tantalum.

Actinium.—The separation of Ac along with lanthanum and possibly other rare earths from uranium minerals or residues has been described on p. 89.

Radio-actinium. — A preparation of actinium (usually with lanthanum or other rare earths) is obtained in solution by dissolving it in strong HNO_3 if necessary. To the solution 10 or 20 milligrams of thorium oxide in the form of nitrate is added to act later as a nucleus.

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The whole is taken to dryness, and the thorium, and with it the RdAc and AcC, are separated from the actinium and lanthanum by two successive precipitations with *m*-nitrobenzoic acid in the usual way. The filtrates and washings are evaporated to dryness and ignited to remove the *m*-nitrobenzoic acid, and the actinium and lanthanum recovered as oxides. This is preferable to adding ammonia to the filtrates and washings, and precipitating the actinium, as the precipitation tends to be incomplete.

Erbium may be substituted for thorium as a nucleus for RdAc if the presence of thorium is considered undesirable, because of its (very slight) activity. The AcC separated simultaneously quickly decays.

RdAc produces AcX, and so the emanation and active deposit of actinium. To free a preparation of RdAc at any time from these products, the following is a useful procedure. Dissolve the thorium or erbium nucleus containing RdAc in HCl (free from H_2SO_4), add a little barium chloride solution, precipitate the thorium and RdAc with excess of ammonia (free from ammonium carbonate) or ammonia gas. AcX remains in solution with the barium, since it is an isotope of radium. Redissolve precipitate, add more barium, and repeat the precipitation with ammonia. Dissolve the precipitate in HCl, add some lead nitrate solution, and saturate with H_2S in the cold. The lead, and with it AcA, AcB, and AcC, are quantitatively precipitated. The RdAc and thorium are then precipitated from the filtrate and washings as hydroxides by the addition of excess of ammonia, and converted if desired, by ignition, into the oxides. It is not necessary to expel the H_2S .

The RdAc so purified is initially free from its products ; actinium X, and with it the emanation and active deposit, are produced in time.

Mesothorium 1.—MsTh1 cannot be separated from its isotope radium. It is obtained from thorium minerals and residues by working them up for barium, with which it separates quantitatively, and then fractionating the MsTh1 from the barium by any of the methods used in fractionating radium.

•Commercial preparations of MsTh1 contain, in addition to its successive products, radium and its products. The reason for that is this. In all thorium minerals a little uranium, and therefore a little radium, is present, consequently the radium and the mesothorium 1 become concentrated together. Radium and its products contribute to the activity of the mesothorium according to the amount separated with it, that is, according to the amount of uranium in the thorium mineral. On account of the long period of radium, the actual amount of it is many times greater than that of the mesothorium 1 separated with it. It thus happens that a preparation of mesothorium 1 containing, perhaps, in relative activity, only 1% of radium is composed actually of 99% radium.

Mesothorium 1 may be separated from a preparation of a thorium salt by dissolving the salt, passing in pure ammonia gas to precipitate the thorium, filtering and washing, and evaporating the filtrate to dryness. This contains the MsTh1, and its isotope ThX, but of course no radium.

Preparations of MsTh1 are convenient sources of MsTh2, RdTh, the emanation and the active deposit

of thorium. The γ -rays from these preparations are used in medical work.

Mesothorium 2.—Since MsTh2 is analogous to lanthanum in properties, and MsTh1 to barium, a separation of one from the other is easily carried out. The presence of the other disintegration products, however, must not be overlooked.

A preparation of MsTh1 freshly made from thorium (free from radium) contains ThX only as radio-active impurity. This body has a period of 3.64 days and MsTh2 of 6.2 hours. The former decays and the latter grows in the preparation, so that 3.64 days after preparation there is 50% of the equilibrium amount of ThX and its products present, and nearly 100% of that of MsTh2. Precipitation of a solution of MsTh1 containing these products with pure ammonia gas brings down ThB, ThC, in addition to MsTh2, and as ThB has a longer period than MsTh2, the latter will not become free from it in time.

The separation is best carried out as follows: To the solution of MsTh1 in HCl add a few milligrams of LaCl_3 , and a few milligrams of PbCl_2 . Pass in H_2S to precipitate the lead (and with it ThB and ThC) completely. Expel H_2S and saturate solution with ammonia gas. The lanthanum and MsTh2 are precipitated quantitatively, the former acting as a nucleus for the latter in filtering; MsTh1 remains in the filtrate. The MsTh2 is free from all radio-active products except the small quantity of RdTh, which has grown since the preparation of the MsTh1. If it be desired, the RdTh may be separated from the MsTh2 and lanthanum by treating it as thorium.

Radiothorium.—RdTh cannot be concentrated from the thorium of minerals, and therefore cannot be separated from minerals directly. Its source is an old preparation of MsTh1 in which it has accumulated from the decay of MsTh2. It is separated free from isotopes from a preparation of mesothorium 1 by treating it as thorium. An old preparation of mesothorium 1 contains the active deposit of thorium, and usually also the active deposit of radium. To the solution in HCl add a small quantity of a lead salt and a small quantity of a thorium or erbium, and of a lanthanum salt. Remove the lead completely with H_2S (and with it the products of the two active deposits), and then precipitate the thorium or erbium and lanthanum with pure ammonia gas. The thorium or erbium acts as a nucleus for the precipitated radiothorium and the mesothorium 2.

Precipitate the thorium or erbium by meta-nitrobenzoic acid in the usual way. The RdTh is precipitated quantitatively with the thorium or erbium nucleus, and the MsTh2 remains in solution with the lanthanum and the mesothorium 1. It is now free from other radio-active bodies, and in a convenient form for any subsequent separation work.

Thorium X.—ThX cannot be obtained free from its isotopes by commencing with thorium minerals or a preparation of thorium (because of the presence of MsTh1) or from a preparation of mesothorium 1 (obviously; also because of the presence in some of Ra). A preparation of radiothorium, free from thorium, obtained by separating it from a preparation of mesothorium 1 in which it has accumulated, is the best

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source. If this be dissolved in HCl and ammonia gas passed in, all the radio-active bodies present except ThX are precipitated. The solution is then evaporated to dryness on the water-bath in a porcelain or silica evaporating-dish, and the ammonium salts ignited in small quantities on the surface on which the film of thorium X is required. If dirt be excluded the film will be very thin. ThX is a convenient source of the emanation and of the active deposit of thorium.

Actinium X.—AcX cannot be obtained pure from minerals because radium, its isotope, is separated with it. It may be obtained pure from a preparation of protactinium and actinium; the latter is the better source as there is yet little accumulation of actinium (and, therefore, of actinium X) in preparations of the former owing to the long half-value period of actinium.

From a preparation of actinium it is separated as follows: The preparation is dissolved in HCl and saturated with ammonia gas. This precipitates the actinium and its rare earth nucleus, and all its products except actinium X. The filtrate and washings are evaporated to dryness on the water-bath in an evaporating-dish; the ammonium salts ignited in small quantities on the surface on which the film of actinium X is required.

AcX is a convenient source of the emanation and active deposit of actinium.

THE ACTIVE DEPOSIT OF RADIUM OF SHORT LIFE.—The bodies included in this title are RaA, RaB, RaC, RaC' and RaC". Their source is the emanation.

If a wire charged negatively to, say, 200 volts be exposed to the emanation, these five bodies become

deposited upon it in time. If the wire be exposed to the emanation for a few seconds only (short exposure) and then removed, the product obtained on it is RaA almost free from the other products; if for five hours (long exposure), the products A, B, and C are in equilibrium. The short exposure is the simplest method of obtaining RaA momentarily pure (but it changes rapidly into RaB, and in twenty minutes has nearly completely disappeared). RaA may also be obtained pure electrochemically by the method similar to that given later for separating polonium from RaD and RaE. Dissolve the active deposit formed by a long exposure in acid. Work quickly. Add to the solution small quantities of solutions of lead, bismuth, and thallium salts. Rotate a plate or button or wire of bismuth in the solution for half a minute, remove, wash and dry. The bismuth contains momentarily pure RaA. The presence of lead, bismuth, and thallium prevent their radio-active isotopes (respectively RaB, RaC, and RaC'') from being deposited on the bismuth.

A (purely) chemical separation of RaA from the other bodies is not practicable owing to the short half-value period of RaA.

RaB may be obtained pure in three ways :

(1) By recoil from RaA.

(2) Electrochemically by v. Hevesy's method.

Dissolve the active deposit from a long exposure off the wire with hot dilute H_2SO_4 , and almost neutralise the solution. Wait twenty minutes to allow the RaA to decay almost completely. Add this solution to a $\frac{\text{N}}{20}$ zinc sulphate solution. Add also a very small quantity

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of bismuth and thallium sulphates. Immerse a plate of zinc in this solution. The potential difference between zinc and solution is about -1.1 volt. Hence nearly pure RaB is deposited upon it. The bismuth and the thallium prevent the deposition of small quantities of RaC and RaC'' respectively.

(3) By any chemical method for separating lead from bismuth and thallium.

RaC may be obtained pure as follows :

(1) By recoil from RaB.

(2) Electrochemically by v. Lerch's or v. Hevesy's method.

Dissolve the active deposit from a long exposure off the wire with hot dilute HCl, almost neutralise the solution, and wait twenty minutes to allow the RaA to decay almost completely. By v. Lerch's method proceed thus: Dip a nickel wire into the solution for a few minutes, remove, wash and dry. The nickel wire has pure RaC upon it. By v. Hevesy's method proceed thus: Almost neutralise the active solution, add it to a normal solution of silver nitrate, and dip a silver wire into this solution for a few minutes, remove, wash and dry. The silver wire has pure RaC upon it.

(3) By any chemical method for separating bismuth from lead and thallium.

RaC'' may be obtained pure as follows :

(1) By recoil from RaC.

(2) Electrochemically by dipping a nickel wire into an HCl solution of RaC and RaC'' containing bismuth. Both RaC and RaC'', when free from bismuth and thallium respectively, are deposited on the nickel wire

in these circumstances. The presence of bismuth in solution, however, prevents the deposition of RaC .

(3) By any chemical method for separating thallium from lead. Chemical methods are not practicable because of the short period of RaC'' .

Radium D.—The sources of RaD are :

(1) Uranium minerals and residues.

(2) Old preparations of radium.

(3) Old emanation tubes, and wires and plates which have been exposed for some time to quantities of emanation.

The first is the richest source because, except in those minerals (such as autunite) from which the lead, and consequently the radium D, has been partly or wholly removed by percolating water and other natural agencies, the radium D is present in equilibrium amount. But the radium D is not pure because it separates with the RaG or end-product of the radium series and any ordinary lead which may be an impurity in the mineral. This mixture, however, is a rich source of RaE and RaF .

In an old preparation of radium which has been sealed up some radium D has accumulated, about 4.2% of the equilibrium amount being produced in the first year and 50% in sixteen years. This may be separated from the radium by adding a little lead salt to the radium solution and separating the lead from the radium as sulphide. The lead contains RaB , RaC , RaC'' , which quickly decay away, and RaE and RaF in addition to the RaD . RaE and RaF may be removed from the RaD either electrochemically or chemically by adding bismuth and thallium salts in solution

to the active solution and separating the lead from bismuth and thallium.

In chemical operations a nucleus for the RaD is necessary. Lead is the best nucleus as it is an isotope. If the presence of lead with the RaD is objectionable, the RaD may be separated from the radium as follows: To the radium solution in HCl add a few milligrams of aluminium chloride in solution and saturated with ammonia gas. Radium remains in the filtrate; with the aluminium are precipitated RaD, RaE, and RaF in addition to RaB, RaC, and RaC'', which quickly decay away. The RaE and RaF can finally be separated from the RaD by v. Lerch's method with nickel, the purified RaD being recovered with the aluminium hydroxide by precipitation from the electrolysed solution with ammonia.

A preparation of radium D is a convenient source, which decays very slowly, of RaE and RaF.

Radium E.—RaE, if separated from its richest source, uranium minerals or residues, is concentrated with its isotope bismuth. Its radio-active isotopes are of relatively quick period and soon decay away. Polonium, however, resembles bismuth chemically, and is therefore usually separated with the radium E.

RaE may, like RaD, be separated from an old preparation of radium. In this case it is first separated along with the lead and the RaD by H_2S , and then separated from RaD by one of the usual methods.

The most convenient source of RaE is a film of RaD, E, and F in an old emanation tube or on a plate of metal. Less convenient is a preparation of RaD, E, and F containing lead, such as is separated from a

uranium mineral or an old preparation of radium, because it may include bismuth, and the presence of bismuth prevents the electro-depositions of its isotope RaE . Electrochemically RaE is separated from RaD by v. Lerch's method with nickel, or v. Hevesy's with silver.

Radium F.—From a solution of RaD , E , and F , RaF is separated by the following ways:

(1) Separate out RaE and RaF by v. Lerch's method with nickel, or v. Hevesy's with silver, or by rotating a disc of copper in the solution for half an hour. Remove the RaF by volatilisation at 900° in air, catching the active material on a metal surface near-by which is water-cooled.

(2) Add lead and bismuth salts in solution to the active solution, and rotate a disc of copper or bismuth, silver or nickel, in it for half an hour. The RaD and RaE are not deposited on the disc because of the presence of their inactive isotopes, and pure RaF is consequently deposited (see also p. 106).

Actinium A, Thorium A, Radium C', Actinium C', Thorium C'.—Owing to the shortness of the periods of these bodies, they have not been prepared nor have their chemical properties been investigated. From their positions in the disintegration series, they are believed to be isotopes of RaA and Po .

Actinium B, Thorium B.—These bodies are prepared from preparations containing them by the methods (2) and (3) given under radium B.

Actinium C, Thorium C.—These bodies are prepared from preparations containing them by the methods (2) and (3) given under radium C.

Actinium C", Thorium C".—AcC" is most easily obtained by recoil from AcC by surrounding a positively-charged needle containing upon it the active deposit of actinium with a negatively-charged cylinder in a vacuum for about seven minutes. If it is desired to obtain the AcC" in solution, the surrounding metal should be a metal like magnesium which is quickly attacked by acids.

ThC" is obtained in an analogous manner. These bodies may be prepared also from AcC and ThC respectively by the three methods described under radium C".

CHAPTER XII

RADIO-ELEMENTS AS INDICATORS, AND THE PROPERTIES OF BODIES AT SMALL CONCENTRATIONS

A LARGE and interesting field of work has been opened up by using radio-active isotopes of common elements to indicate what is occurring to the latter in chemical operations. Different properties of compounds of an element like lead or thallium, which has radio-active isotopes, may be investigated at extremely small concentrations by using the radio-active properties of the isotopes for purposes of identification and measurement. The concentration at which a radio-active body can be quantitatively estimated by the methods of radio-activity is, of course, many times less than by the methods of spectroscopy, which are the most refined ways of detecting and estimating inactive substances. By assuming that the radio-active body has exactly the same chemical and physical properties as its inactive isotope, the properties of the inactive body may be investigated in concentrations down to the extreme limit at which the most sensitive radio-active isotope can be detected. For example, 10^{-11} milligram of ThB can be detected by the methods of radio-activity; therefore the properties of lead at this concentration may be investigated.

The qualities necessary for a good radio-active indicator are :

(1) Its radio-activity should be distinctive and be capable of easy measurement.

(2) Its half-value period must not be so short that chemical operations must be unduly hurried to prevent the almost total decay of the body before the experiment is concluded.

It is not always possible to obtain these qualities in an indicator, but as there is often a choice of indicators for one substance, they help to fix the most expedient one.

In the table on p. 161 are given the substances whose properties may be investigated by the help of radio-active indicators, with some notes on their detection.

The following are some of the properties of these bodies that have been investigated with radio-active indicators.

(1) Solubilities of difficultly soluble salts.

(2) The volatility of different compounds at small concentrations.

(3) The rate of diffusion of an atom (or a molecule) of a metal in a block of itself, or of a metal ion in a crystalline compound of the metal.

(4) The existence of new compounds.

The solubilities of salts.—These are determined directly. An experiment is carried out as follows : A large quantity of indicator is accurately determined by electroscopic measurements. It is put into solution and added to a solution of a compound containing the metal of the compound whose solubility is under investigation, and thoroughly stirred. The difficultly

TABLE 13

<i>Substance to be investigated.</i>	<i>Possible indicators.</i>	<i>How detected.</i>	<i>Notes.</i>
Protactinium	UX ₂	By its own radiations	Period inconveniently short.
Actinium .	MsTh ₂	By its own radiations.	
Thorium .	UX ₁	By its own radiations and those of UX ₂	UX ₁ is the most convenient.
	RdAc } RdTh }	By the radiations of itself and products in equilibrium	
Radium .	MsTh ₁	By the amount of MsTh ₂ formed.	
	AcX } ThX }	By the radiations of itself and products in equilibrium.	
Bismuth .	RaC	By radiations from RaC, C', C"	ThC and RaE are the most convenient because of their periods.
	AcC	" " " AcC, C', C"	
	ThC	" " " ThC, C', C"	
	RaE	By its own radiations	
Lead .	RaB } AcB } ThB } RaD }	By the amount of the C, C', C" formed from the B body in a given time By amount of RaE formed in a given time.	RaB is the least convenient.
Thallium .	RaC" } AcC" } ThC" }	By their own radiations	All the periods are inconveniently short. AcC" is the most convenient.

soluble compound is then quantitatively precipitated with its radio-active isotope from the solution, washed, dried, and weighed. The salt is next shaken up with water at a given temperature until the solution is saturated with it. The same fraction of the indicator as of the salt goes into solution. The known volume of water is then filtered from the salt, evaporated to dryness, and the amount of the indicator determined accurately by electroscopic measurements. The solubility of the indicator is then calculated in the ordinary way, and this is the solubility of the difficultly soluble compound.

This method works excellently for difficultly soluble salts like PbCrO_4 and PbS , whose solubilities cannot be measured properly by the direct method, and which are usually measured indirectly—for example, by measurements of electrical conductivity.

Hevesy, Paneth, and Frl. Róna determined the solubility of lead chromate by the method above, using RaD as indicator, and found its solubility to be 2×10^{-7} mol. per litre.

The method applies to all the compounds of the bodies tabulated in Table 13, but is limited to these. Needless to say, when it is applied to an investigation of the solubility of easily soluble compounds like PbCl_2 , which are determined by the usual methods, it gives an equally accurate result.

Volatility of compounds at small concentrations.
—The volatility of lead, lead oxide, and the halogen and other salts of lead may be studied when these bodies are in extremely small concentration by studying the volatility of radium B in different circumstances.

Experiments are usually carried out by exposing a plate of metal to the radium emanation for five hours, determining its activity when the radium A has decayed away, placing it in an electric furnace which is kept uniformly at a given temperature, and carrying out the volatilisation in the atmospheres of different gases. In hydrogen, radium B exists probably as the metal, in oxygen as oxide, in chlorine as chloride, etc. The volatility of compounds of bismuth may be studied similarly by working with RaC, ThC, AcC, or RaE. The method is, obviously, applicable to any body with a radio-active isotope whose compounds can be conveniently estimated by the methods of radio-activity.

Diffusion experiments. — Radio-active isotopes have been used to determine the velocity of diffusion of molecules and ions among themselves. The rate of diffusion is known to be dependent on the molecular diameter (which is the same for all isotopes of one element), and not on the mass, so that a radio-active body diffusing among the molecules of an inactive isotope affords a means of investigating the velocity of diffusion of molecules among themselves. V. Hevesy has done this for lead. At the bottom of a narrow, vertical tube he placed a layer of lead throughout which ThB was uniformly distributed, and on top of this a layer of (inactive) lead three times as thick. The whole was kept at 343° for two days. The mass was then allowed to cool, and later cut up into four equal sections. In each of these the radio-activity of ThB was determined, and from the results its distribution throughout the total mass was obtained. The mean value of the coefficient of diffusion of ThB

in lead, *i.e.* of lead in itself, at 343° was found to be 2.2 square centimetres per day.

It is obvious that this method has a wide application in measuring the rate of diffusion of the molecules of lead, thallium, bismuth, and other elements with radio-active isotopes in themselves; also of the ions of these elements in their compounds.

The existence of new compounds.—The existence of BiH_3 and of a hydride of lead has been shown by the use of indicators. BiH_3 corresponds to AsH_3 and SbH_3 , but has only recently been prepared. Paneth demonstrated its existence as follows: He collected the active deposit of thorium ($\text{ThB} + \text{ThC}$) on thin magnesium and dissolved the whole in dilute HCl . The gases evolved were passed through cotton-wool into an evacuated electroscope. The gas in the electroscope was found to decay with the period of ThC , showing that, in addition to hydrogen, a gaseous product of ThC had been evolved. This is very probably $\text{ThC} \cdot \text{H}_3$, and since ThC is an isotope, the method indicates how BiH_3 may be prepared. Paneth found that only one or two parts per thousand of the ThC on the magnesium combined with hydrogen in this way, which indicates the difficulty of forming $\text{ThC} \cdot \text{H}_3$ (and therefore of BiH_3) by this method. Having thus shown the existence of BiH_3 by a radio-active indicator, Paneth succeeded further in preparing this compound by ordinary means. In a similar way he has succeeded in preparing a hydride of lead.

The active deposit and the determination of potential differences.—In the discussion of electrochemical methods of separating the members of an

active deposit, the interesting relation, discovered by v. Hevesy, has been pointed out. He connected the potential difference between a metal and a solution containing the active deposit in equilibrium into which it is dipped, and the relative amounts of RaB and RaC (or AcB and AcC or ThB and ThC) deposited upon it from solution.

This relation enables single potential differences

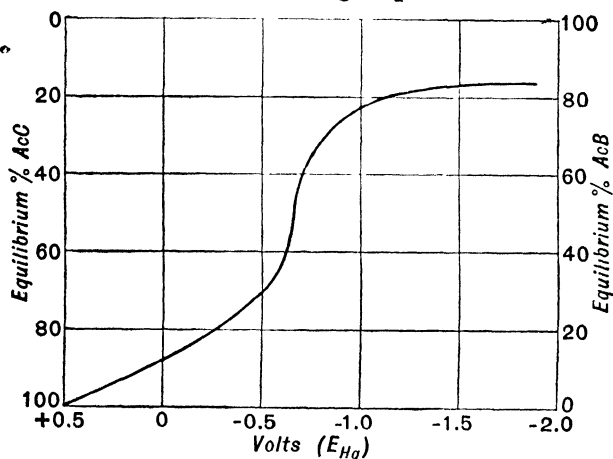


FIG. 12.

to be determined with fair accuracy, and some of the results obtained will now be given.

The method of experiment is as follows :

An accurate curve—that shown in Fig. 12, above—is first obtained by plotting the equilibrium percentages of AcB and AcC (the most convenient pair of B and C bodies for this purpose) as ordinates against the potential differences necessary for their deposition as abscissæ.

Next AcB and AcC in equilibrium are added to the solution between a metal and which the potential difference is required. The metal is then immersed for a definite time, usually one minute, removed, washed and dried, and the percentages of AcB and AcC deposited upon it determined by electroscopic measurements. When this result is obtained, the potential difference between metal and solution is read off from the curve.

In this way v. Hevesy obtained several new and interesting results, some of which are tabulated below.

TABLE 14

No.	System studied.	Potential difference in volts against the calomel electrode obtained by radio-active method.	Potential difference obtained by usual electrical method.
1	Ta/Ta ₂ O ₅	0.00	0.05
2	Ta/N. KCl	- 0.03	- 0.04
3	Cu/ $\frac{N}{2}$. CuSO ₄	...	+ 0.02
4	Cu/water	- 0.7	...
5	Cd/ $\frac{N}{2}$. CdSO ₄	...	- 0.71
6	Ni/N. NiSO ₄	...	about - 0.53
7	Ni/NiCl ₂	about + 0.5	...
8	Cu/water for 0.2 sec.	- 2.0	...
9	Cu/water for 60 secs.	- 0.7	...

Results 1 and 2 show the close agreement between the results obtained by the two methods. Results 3 and 4 show the large difference between a definite system and an indefinite one. When copper is dipped into a seminormal solution of its sulphate, about 87% of AcC and 13% of AcB are deposited. When dipped into water the percentages are 60 and 40. The difference

in potential exhibited by a metal when dipped into a solution containing its own ions, and when dipped into one which initially does not contain them, is of course well known. The discordancies obtained by early workers on the electrochemical separation of the components of the active deposit were due, however, to the fact that they had overlooked this difference. It is seen from results 4 and 5 that the potential between copper and water is that between cadmium and a seminormal solution of its sulphate.

Results 6 and 7 point out the effect of the passivity of nickel. The normal potential of nickel is -0.53 volt. If nickel be rendered passive, however, as it is when dipped into a hydrochloric acid solution, its potential becomes approximately $+0.5$ volt, because on it is then deposited nearly pure C. The degree of passivity of nickel due to certain reagents may be conveniently and quickly measured by the radioactive method. On nickel rendered slightly passive was found to be deposited approximately 75% of the equilibrium amount of AcC. This corresponds, as the curve shows, to a potential difference of about -0.4 volt; when rendered more passive it was proved that 90% of AcC was deposited on it. This corresponds to a potential difference of $+0.1$ volt. The radioactive method should have a wide application in studying the passivity of metals. Results 8 and 9 show the effect of time of immersion of a metal in a given solution on the potential difference set up. Nernst's fundamental formula, $E = -RT \log_e \frac{C}{c}$, where c is the concentration of the ions of the metal present in

the liquid surrounding the electrode, indicates that if a metal be immersed in water the potential difference initially must be $-\infty$, since c initially is zero, and must fall rapidly as metal ions are produced till a constant result is obtained. The potential difference $-\infty$ cannot be determined, however, in terms of the percentages of B and C, nor is it practicable to immerse a plate in the active solution for less than 0.2 second. A quantitative comparison of theory and experiment is thus not possible by the radio-active method, but the results obtained bear out this consequence of Nernst's formula qualitatively. It was found experimentally that the potential difference between metal and water fell rapidly in the first few seconds, and attained thereafter an unchanging value.

The precipitation and adsorption of radio-active substances.—Fajans and Richter came to the following conclusion from experiments which they conducted on the precipitation of radio-elements by different reagents: there is a direct relation between the percentage of a radio-element which is precipitated along with an inactive body from a solution, and the solubility of the compound of the radio-element with the acid radicle of the inactive body.

For example, thorium B, an isotope of lead, was precipitated almost quantitatively when bismuth sulphide, manganese carbonate, or barium sulphate were precipitated from a solution containing thorium B; it was only partially precipitated when silver iodide and silver chloride were precipitated from solution, and practically not at all when nitron nitrate was precipitated. Now lead sulphide, carbonate, and sulphate

are extremely insoluble salts ; the iodide and chloride are much more soluble, and the nitrate is very soluble. Paneth and Horovitz have put forward a conclusion with regard to the adsorption of radio-elements somewhat similar to that of Fajans and Richter with respect to precipitation. They found a relation between the amount of a radio-element which is adsorbed by a body and the insolubility in the solution of the compound formed by the radio-element and the acid radicle of the adsorbing body.

The acid radicle which with the radio-element forms the insoluble compound must be present in the adsorbing body ; it is not sufficient for it to be in solution. An example may make this clear. Lead sulphate is a fairly insoluble body in aqueous solution, hence, according to the rule above, thorium B, an isotope of lead, should be almost completely removed from a solution containing it by shaking the solution with barium sulphate powder. If, however, ammonium sulphate solution be added to that containing thorium B, and nitron nitrate powder shaken up in it, there is no adsorption of the thorium B by nitron nitrate, because lead nitrate is very soluble, and because the sulphate radicle is in solution and not in the adsorbing body.

It is clear that the conclusion of Fajans and Richter may be deduced from that of Paneth and Horovitz, and that both open up an interesting field of work in throwing light on the connection between the power of being adsorbed and the purely chemical properties of bodies at extremely minute concentrations.

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