Bakerian Lecture: The Succession of Changes in Radioactive Bodies

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V. Bakerian Lecture.—*The Succession of Changes in Radioactive Bodies*.

By Professor E. Rutherford, *F.R.S., Macdonald Professor of Physics, McGill University, Montreal.*

1. In previous papers by Rutherford and Soddy* it has been shown that the radioactivity of the radio-elements is always accompanied by the production of a series of new substances with some distinctive physical and chemical properties. For example, thorium produces from itself an intensely radioactive substance, ThX, which can be separated from the thorium in consequence of its solubility in ammonia. In addition, thorium gives rise to a gaseous product, the thorium emanation, and also to another substance which is deposited on the surface of bodies in the neighbourhood of the thorium, where it gives rise to the phenomenon known as 'excited activity.'

A close examination of the origin of these products shows that they are not produced simultaneously, but arise in consequence of a succession of changes originating in the radio-element. Thorium first of all gives rise to the product ThX. The ThX produces from itself the thorium emanation, and this in turn is transformed into a non-volatile substance. A similar series of changes is observed in radium, with the exception that there is no product in radium corresponding to the ThX in the case of thorium. Radium first of all produces an emanation, which, like thorium, is transformed into a non-volatile substance. In uranium only one product, UrX, has been observed, for uranium does not give off an emanation and does not in consequence produce excited activity on bodies.

2. As a typical example of the evidence, from which it is deduced that one substance is the parent of another, we will consider the connection of the two products ThX and the thorium emanation. After the separation of ThX from a thorium solution, by precipitation with ammonia, the precipitated thorium hydroxide has lost to a large extent its power of emanating. This cannot be ascribed to a prevention of escape of the emanation produced in it, for very little emanation is observed when a current of air is drawn through the hydroxide in a state of solution,

* 'Phil. Mag.,' Sept., Nov., 1902; April and May, 1903.

when most of the emanation present would be carried off. On the other hand, the solution containing the ThX gives off a large quantity of emanation, showing that the power of giving an emanation belongs to the product ThX. Now it is found that the quantity of emanation given off by the separated ThX decreases according to an exponential law with the time, falling to half value in four days. The rate of production of emanation thus falls off according to the same law and at the same rate as the activity of the ThX measured in the ordinary manner by the α rays. Now this is exactly the result to be expected if the ThX is the parent of the emanation, for the activity of ThX at any time is proportional to its rate of change, i.e., to the rate of production of the secondary type of matter by the emanation in consequence of a change in it. Since the rate of change of the emanation (half transformed in 1 minute) is very rapid compared with the rate of change of ThX, the amount of emanation present will be practically proportional to the activity of the ThX at any instant, i.e., to the amount of unchanged ThX present. The observed fact that the hydroxide regains its power of emanating in the course of time is due to the production of fresh ThX by the thorium, which in turn produces the emanation.

In a similar way, excited activity is produced on bodies over which the emanation is passed, and in amount proportional to the activity of the emanation, i.e., to the amount of the emanation present. This shows that the active deposit, which gives rise to the phenomenon of excited activity, is itself a product of the emanation. The evidence thus seems to be conclusive that ThX is the parent of the emanation and that the emanation is the parent of the deposited matter.

3. Each of these radioactive products is marked by some distinctive chemical and physical properties which differentiates it from the preceding and succeeding products. For example, ThX behaves as a solid and is soluble in ammonia, while thorium is not. The thorium emanation behaves as a chemically inert gas and condenses at a temperature of $-120°$ C. The active deposit from the emanation behaves as a solid and is readily soluble in sulphuric and hydrochloric acids and is only slightly soluble in ammonia. The two emanations and the products, UrX and ThX, lose their activity according to an exponential law with the time, and at a rate that is independent—as far as observation has gone—of the chemical and physical agents at our disposal. The time taken for the radioactivity of each of these products to fall to half its value is thus a definite physical constant, which serves to distinguish it from all other products.

On the other hand, the 'excited activity' produced in bodies by exposure in the presence of the thorium and radium and actinium emanations does not decay according to a simple exponential law. The variation of the excited activity with time is very complicated, especially in the case of radium, and is dependent on the time of exposure of the body in the presence of the emanation.

It will be shown in the paper that the complicated rate of decay of the excited activity of the thorium, radium, and actinium is due to the fact that the deposited

matter undergoes two successive changes in thorium and actinium and at least four successive changes in radium.

The changes occurring present several points of interest and importance and will be considered in some detail. In the course of this paper the following subjects will be considered :—

(1) Nomenclature ;

(2) Rate of decay of the excited activity of thorium and radium for different times of exposure to the emanation, and for the different types of radiation ;

(3) Mathematical theory of successive changes ;

(4) Application of the theory to explain the changes in (*a*) thorium, (*b*) actinium, (*c*) radium ;

(5) Matter of slow rate of change produced by radium : comparison of the matter with the radio-tellurium of MARCKWALD ;

(6) Apparent radioactivity of ordinary matter, due in part to an active deposit of slow rate of change from the atmosphere ;

(7) Comparison of the successive changes in uranium, thorium, actinium, and radium ;
Table of active products ;

(8) Discussion of the significance of 'rayless' changes in the radio-elements.

(9) Radiations from the active products ;
Significance of the appearance of β and γ rays in the last rapid change in the radio-elements ;

(10) Difference between radioactive and chemical change ;

(11) Discussion of experiments made to measure the charge carried off by the α rays ;

(12) Magnitude of the changes occurring in the radio-elements ;
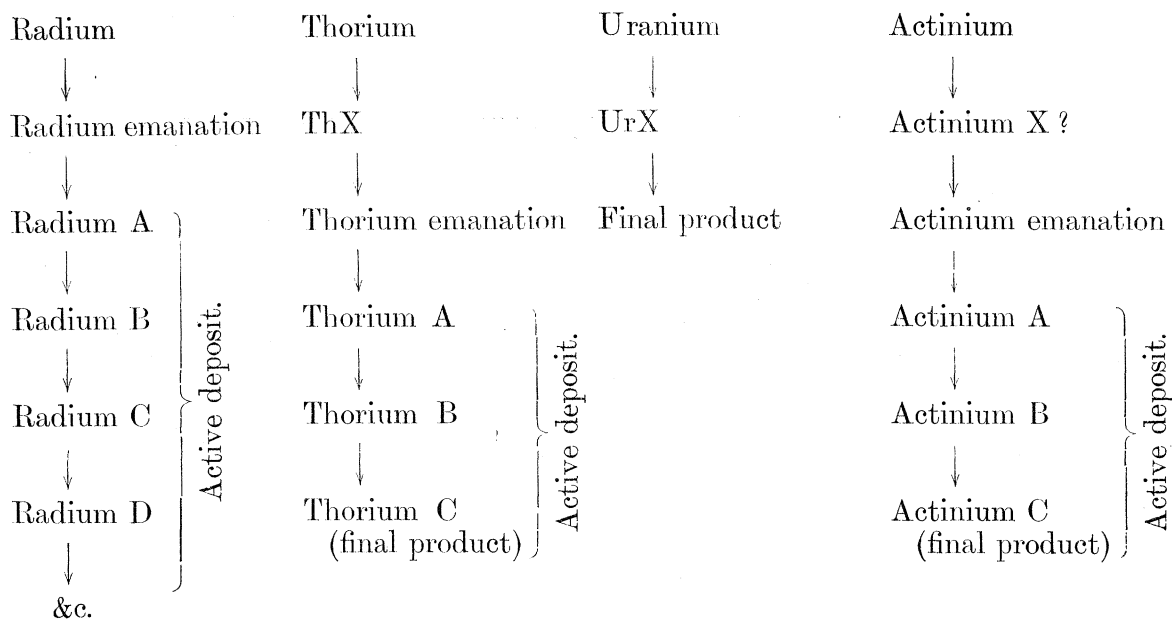
(13) Origin of the radio-elements.

4. *Nomenclature.*—The nomenclature to be applied to the numerous radioactive products is a question of great importance and also one of considerable difficulty. Since there are at least six distinct substances produced from radium, and probably five from thorium and actinium, it is neither advisable nor convenient to give each a

special name. At the same time, it is becoming more and more necessary that each product should be labelled in such a way as to indicate its place in the succession of changes. This difficulty is especially felt in discussing the numerous changes in the active deposits from the different emanations. Many of the names attached to the products were given at the time of their discovery, before their position in the scheme of changes was understood. In this way the names UrX, ThX were applied to the active residues obtained by chemical treatment of uranium and thorium. Since, in all probability, these products are the first products of the two elements, it may be advisable to retain these names, which certainly have the advantage of brevity. The name 'emanation' was originally given to the radioactive gas from thorium, and has since been applied to the similar gaseous products of radium and actinium.

Finding the name 'radium emanation' somewhat long and clumsy, Sir WILLIAM RAMSAY* has recently suggested 'ex-radio' as an equivalent. This name is certainly brief and is also suggestive of its origin; but at least four other ex-radios, whose parentage is as certain as that of the emanation, remain unnamed. A difficulty arises in applying the corresponding names ex-thorio, ex-actinio to the other gaseous products, for, unlike radium, the emanations of thorium and actinium are probably the second and not the first disintegration product of the radio-elements in question. Another name thus has to be applied to the first product in these cases. It may be advisable to give a special name to the emanation, as it so far has been the product most investigated and the first to be chemically isolated; but, on the other hand, the name 'radium emanation' is historically interesting, and suggests a type of volatile or gaseous matter. Since the term 'excited' or 'induced' activity refers only to the radiations from the active body, a name is required for the radiating matter itself. The writer some time ago suggested the name 'emanation X.'† This title was given from analogy to the names UrX and ThX, to indicate that the active matter was product of the emanation. The name, however, is not very suitable, and, in addition, can only be applied to the initial product deposited, and not to the further products of its decomposition. It is very convenient in discussing mathematically the theory of successive changes to suppose that the deposited matter called A is changed into B, B into C, C into D, and so on. I have therefore discarded the name emanation X, and have used the terms radium A, radium B, and so on, to signify the successive products of the decomposition of the emanation of radium. A similar nomenclature is applied to thorium and actinium. This system of notation is elastic and simple, and I have found it of great convenience in the discussion of successive products. In speaking generally of the active matter, which causes excited activity, without regard to its constituents, I have used the term 'active deposit.' The scheme of nomenclature employed in the paper is clearly shown below:—

* 'Proc. Roy. Soc.,' p. 470, June, 1904; 'Comptes Rendus,' 138, June 6, 1904.
† 'Phil. Mag.,' February, 1904.

Radium	Thorium	Uranium	Actinium
↓	↓	↓	↓
Radium emanation	ThX	UrX	Actinium X ?
↓	↓	↓	↓
Radium A	Thorium emanation	Final product	Actinium emanation
↓	↓		↓
Radium B	Thorium A		Actinium A
↓	↓		↓
Radium C	Thorium B		Actinium B
↓	↓		↓
Radium D	Thorium C (final product)		Actinium C (final product)
↓			
&c.			

(Radium A–D bracketed: Active deposit. Thorium A–C bracketed: Active deposit. Actinium A–C bracketed: Active deposit.)

Each product on this scheme is the parent of the product below it. Since only two products have been observed in the active deposit of thorium and actinium, thorium C and actinium C respectively refer to their final inactive products.

5. *Decay of the Excited Activity of Thorium.*—If a body is exposed for several days in the presence of a constant supply of thorium emanation, the activity imparted to it reaches a constant value. On removal, the activity is found to decay very approximately according to an exponential law with the time, falling to half value in 11 hours. If, however, the body is only exposed for a few minutes in the presence of the emanation, the activity after removal increases, during the course of about 3 hours, to 5 to 6 times the initial value, passes through a maximum, and then decays approximately according to the normal rate, *i.e.*, the activity falls to half value in about 11 hours.*

The curve of increase of activity with time (measured by the α rays) for a rod exposed 10 minutes in the presence of the thorium emanation is shown graphically in fig. 1, curve C. The rod was made active by charging it negatively to 100 volts in a closed vessel.† With increasing times of exposure, the rise of the excited activity after removal becomes less and less marked, and is almost inappreciable after 6 hours.

I have discussed elsewhere in some detail ('Treatise on Radioactivity,' p. 258) the explanation of this remarkable effect, and have shown that it can be accounted for

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* RUTHERFORD, 'Phil. Mag.,' January, 1903.

† It is important that the air in the vessel should be dust-free, for Miss BROOKS has found that the carriers of 'excited activity' in dusty air adhere to the dust particles, and remain anchored in the gas for several days. On the application of an electric field, some of the dust particles are conveyed to the negative electrode. The presence of old radioactive matter in the rod masks, to a large extent, the rise observed for the radioactive matter which has just been formed
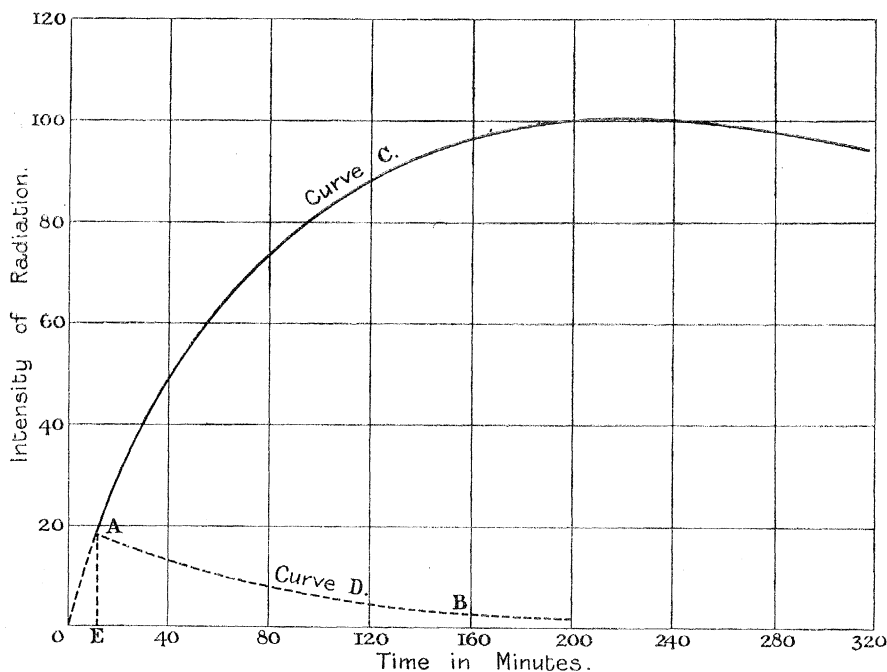
Fig. 1.

completely on the supposition that there are two successive changes occurring in the matter deposited by the emanation, viz. :—

(1) A 'rayless' change, in which the matter undergoes a transformation according to the same law as the radioactive changes, but which is not accompanied by the appearance of either α or β rays.

(2) A second change which gives rise to all three types of rays.

It will be shown later (section 13) that the matter in the two changes is half transformed in 55 minutes and 11 hours, respectively; but without further physical data it is not possible to deduce directly from the experimental curves whether the first change has the period 55 minutes, or 11 hours. It is supposed that the matter A, deposited from the emanation, changes into the matter B, and this in turn changes into C. The change from A to B is not accompanied by any observable radiation, while the change from B to C is accompanied by all three types of rays. The matter C is either inactive or active to such a slight extent that its radioactivity cannot be detected.

The theory of these numerous changes will be considered in detail, later, together with the corresponding changes in radium and actinium.

6. *Decay of the Excited Activity of Radium.*—Miss BROOKS and the writer[*] showed that the curves of decay of the excited activity of radium were very complicated in character and varied greatly with the time of exposure. It was later pointed out that this was probably due to a triple change in the deposited matter.

* 'Phil. Mag.,' July, 1902.

P. CURIE and DANNE* recently determined the curves of decay of the excited activity of radium for different times of exposure. A discussion of their results will be given later.

The shape of the decay curves of the excited activity of radium depends not only on the time of exposure, but also on which of the types of radiation is used as a means of measurement. The curves of decay of excited activity are quite different for the α and for the β rays.

In the experiments a radium solution was placed in a closed glass vessel (see fig. 2, A). The emanation then collected in the air space above the solution. The rod to be made active was introduced through an opening in the stopper and exposed in the
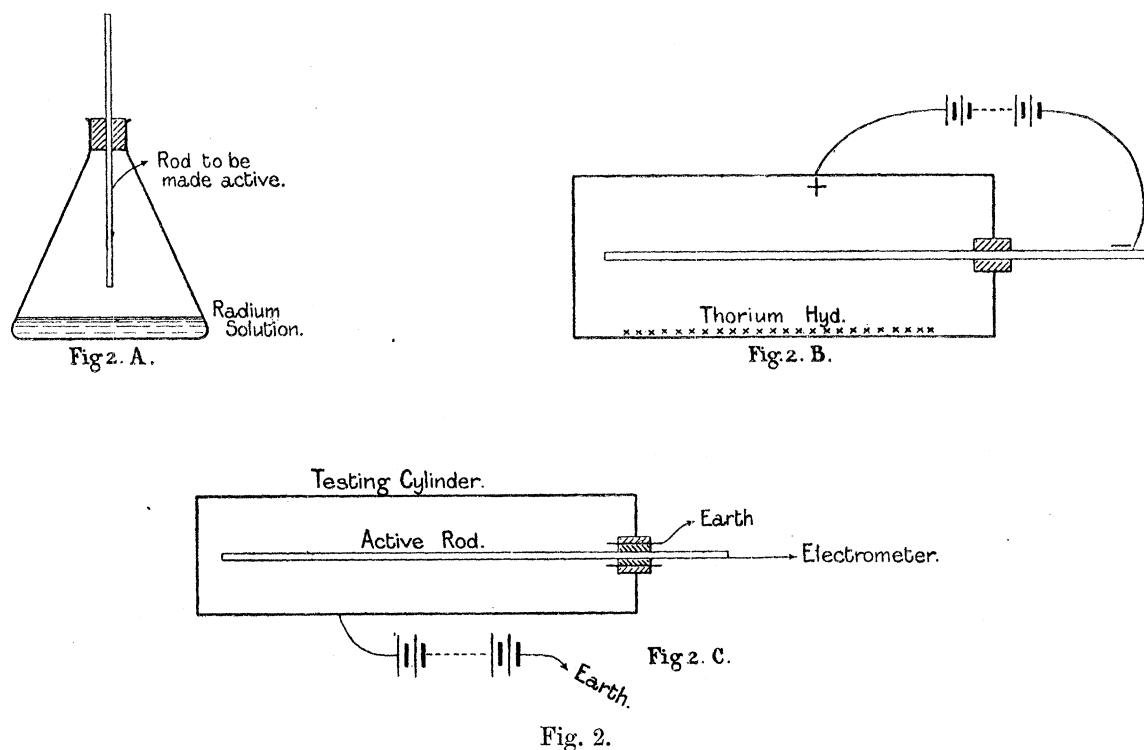
Fig. 2.

presence of the emanation for a definite interval. For experiments on the excited activity of thorium, some highly emanating thorium hydroxide was placed inside a closed cylinder (see fig. 2, B). The central rod, which was to be made active, was connected to the negative pole of a battery of about 100 volts. If the decay of activity was to be measured by the α rays, the rod was made the central electrode in a cylindrical vessel (see fig. 2, C). A saturating voltage was applied, and the current between the cylinders measured by means of an electrometer with a suitable capacity in parallel. A current of dust-free air was continuously circulated through the cylinder in order to remove any emanation which might have adhered to the wire. For experiments on the β or γ rays it was found advisable to use an electroscope instead

* 'Comptes Rendus,' 136, p. 364, 1903.

of an electrometer.   The gold-leaf system was insulated inside of a metal vessel by means of a sulphur bead, after the method first employed by C. T. R. WILSON
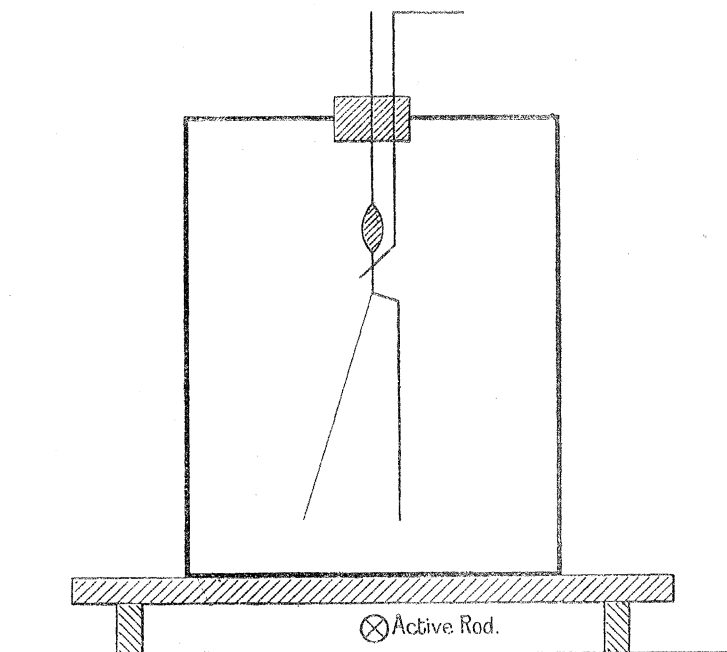

Fig. 3.

(see fig. 3).   The rate of movement of the leaves was determined through mica windows by means of a microscope provided with a micrometer eye-piece.   For
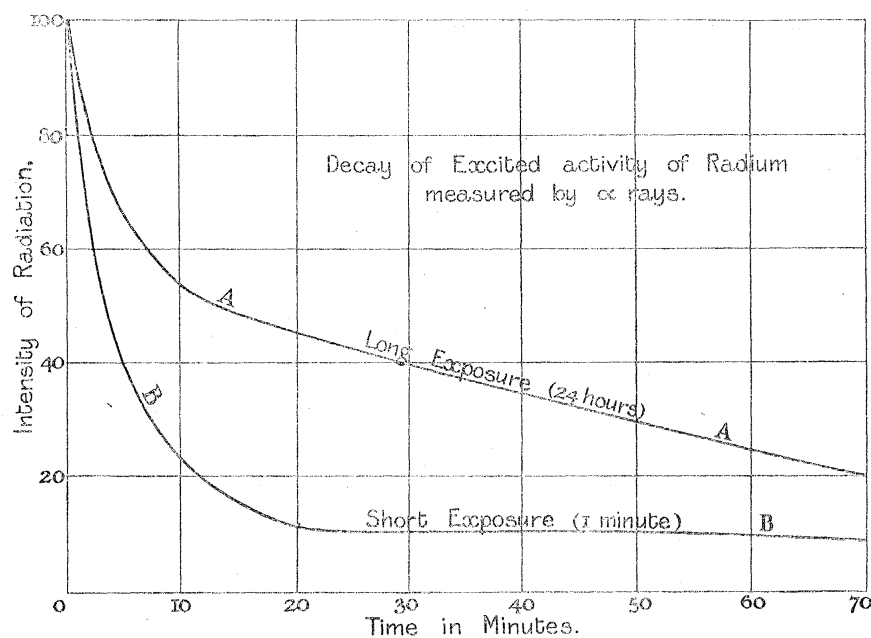

Fig. 4.

measurements with the β rays, the active rod was placed under the electroscope, and, before entering into the vessel, passed through a sheet of metal of sufficient thickness

to absorb all the α rays. For measurements with the γ rays, the electroscope was placed on a lead plate 0·6 centim. thick, and the active rod placed under the lead plate. The α and β rays were completely stopped by the lead, and the discharge in the electroscope was then due to the γ rays alone. The electroscope is very advantageous for measurements of this character, and accurate observations can be simply and readily made. It, however, cannot be used with advantage to follow very rapid changes in activity.

7. The curve of decay of activity, measured by the α rays, for an exposure of 1 minute in the presence of the radium emanation is shown in fig. 4, curve BB.

The curve exhibits three stages :—

(1) A rapid decay in the course of 15 minutes to less than 10 per cent. of the value immediately after removal ;
(2) A period of 30 minutes in which the activity varies very little ;
(3) A gradual decrease almost to zero.

The initial drop decays very approximately according to an exponential law with the time, falling to half value in about 3 minutes. Three or 4 hours after removal the activity again decays according to an exponential law with the time, falling to half value in about 28 minutes. These results thus indicate :—

(1) An initial change in which half the matter is transformed in 3 minutes ;
(2) A final change in which half the matter is transformed in 28 minutes.

Before considering the explanation of the intermediate portion of the curve further experimental results will be considered.

The curve of decay of the excited activity for a long exposure (24 hours) is shown graphically in fig. 4, curve AA. There is at first a rapid decrease for the first 15 minutes to about 50 per cent. of the initial value, then a slower decay, and after an interval of about 4 hours a gradual decay nearly to zero, according to an exponential law with the time, falling to half value in 28 minutes.

The curves of variation with time of the excited activity when measured by the β rays are shown graphically in figs. 5 and 6.

Fig. 5 is for a short exposure of 1 minute. Fig. 6 shows the decay for a long exposure of about 24 hours.

The curves obtained for the β rays are quite different from those obtained for the α rays. For a short exposure, the activity measured by the β rays is at first small, then passes through a maximum about 36 minutes after removal. There is then a gradual decrease, and after several hours the activity decays according to an exponential law, falling, as in the other cases, to half value in 28 minutes.

The curve shown in fig. 6 for the β rays is very similar in shape to the corresponding curve, fig. 4, curve AA, for the α rays, with the exception that the rapid initial drop observed for the α-ray curve is quite absent. The later portions of the

curve are similar in shape, and, disregarding the first 15 minutes after removal, the activity decays at exactly the same rate in both cases.
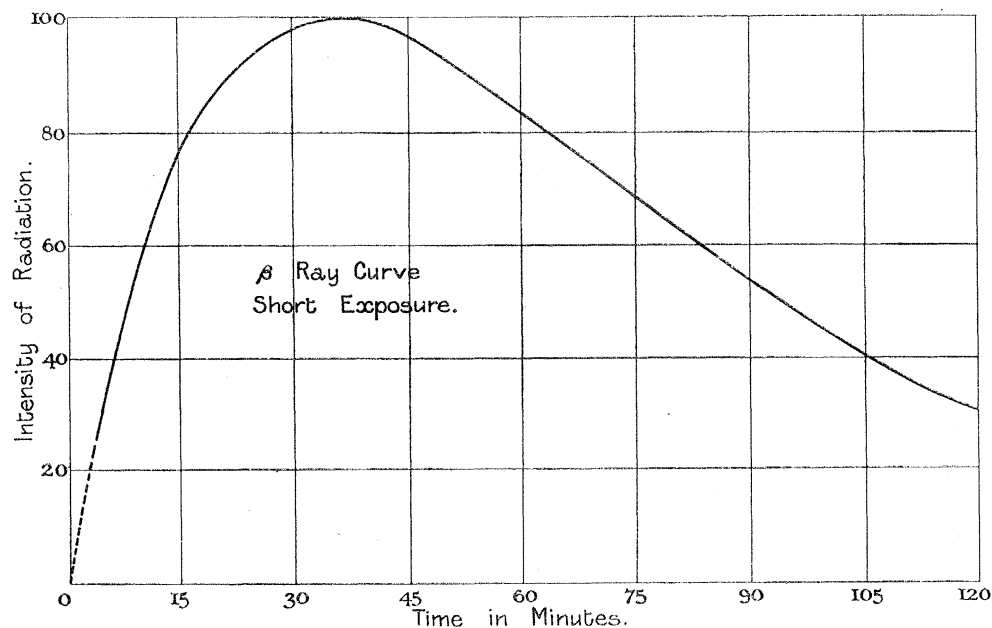
Fig. 5.

The curves obtained by means of the γ rays are identical with those obtained for the β rays. This shows that the β and γ rays always occur together and in the same proportion.
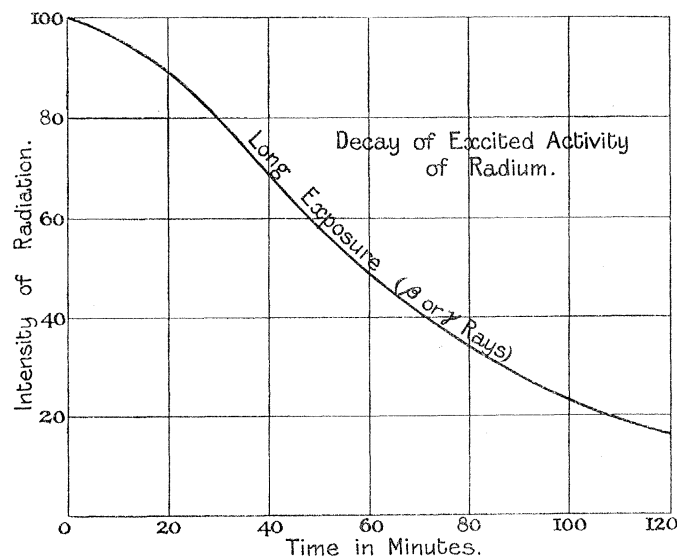

Fig. 6.

For increase of the time of exposure from 1 minute to 24 hours the curves obtained are intermediate in shape between the two representative limiting curves, figs. 5 and 6.

The results obtained by CURIE and DANNE for the decay of the excited activity of radium for different times of exposure are shown graphically in fig. 7. The ordinates
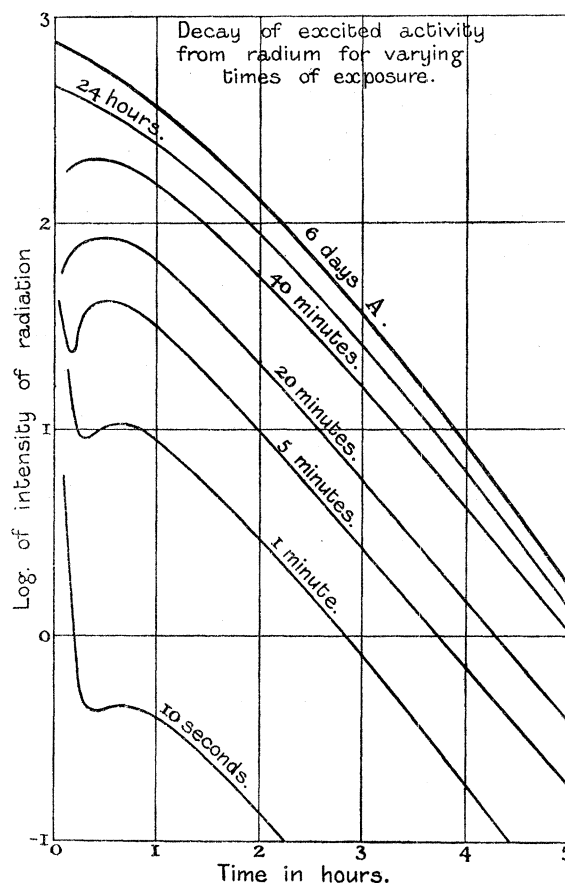

Fig. 7.

represent the logarithm of the activity and the abscissæ time in hours. A comparison of the curves obtained by myself and those obtained by CURIE and DANNE at once discloses some marked differences.

The lowest curve for a short exposure of 20 seconds is very similar in shape to the corresponding curve, fig. 4, curve B, where the activity was measured by the α rays. On the other hand, the upper curve A of fig. 7 does not show the initial drop found by me (see fig. 4, curve A), where the activity is measured by the α rays. If the activity is supposed to be measured by the β rays, the upper curve A, fig. 7, is similar to that shown in fig. 6. The lower curve of fig. 7 is, however, again different from the corresponding β-ray curve shown in fig. 5.

I think the difference between the results of CURIE and DANNE and those obtained by myself lies in the fact that the former did not take into account that the shape of the curves depended on whether the α or β rays were used as a means of measurement. CURIE and DANNE do not state, or give any evidence to show, which of the types of rays they employed for measurement, but I think there is no doubt that the lower

curve (fig. 1) was obtained by means of the α rays, while the four upper curves (fig. 7) were obtained by means of the β rays. The intermediate curves, for an exposure of 1 minute and 5 minutes, do not agree with the results obtained by me for either the α or β rays, but appear to be a mixture of both.

The sudden initial drop is a characteristic of the α-ray curve, but I have only observed the rise to a maximum, as in fig. 5, where measurements are made by the β or γ rays.

Miss BROOKS, working in the laboratory, has re-determined the cause of decay of the excited activity of radium for different times of exposure, separately for both the α and β rays, and the results will be published shortly.*

8. *Explanation of the Curves.*—It has been pointed out that the rapid initial drop for curves A and B, fig. 4, is due to a change giving rise to α rays, in which half of the matter is transformed in about 3 minutes. The absence of the drop in the corresponding curves, when measured by the β rays, shows that the first 3-minute change does not give rise to β rays; for if it gave rise to β rays, the activity should fall off at the same rate as the corresponding α-ray curve.

It has been shown that the activity several hours after removal decays in all cases according to an exponential law with the time, falling to half value in 28 minutes. This is the case whether for a short or long exposure, or whether the activity is measured by the α, β, or γ rays. This indicates that the final 28-minute change gives rise to all three types of rays.

It will be shown that these results can be completely explained on the supposition that three successive changes occur in the deposited matter of the following character† :—

(1) A first change of the matter deposited in which half of the matter is transformed in about 3 minutes, and which gives rise only to α rays;

[* Since published, 'Phil. Mag.,' September, 1904.]

† The view that the complicated rates of decay of the excited activity produced by radium and thorium were due to a double change in the deposit from thorium and a treble change in that of radium was first suggested in 1902 (RUTHERFORD, 'Physik. Zeitsch.,' 3, p. 254, 1902), and discussed later in 'Phil. Mag.,' Jan., 1903, and also by RUTHERFORD and SODDY, 'Phil. Mag.,' April and May, 1903. In 1903, CURIE and DANNE ('Comptes Rendus,' 136, p. 364, 1903) found that the decay curve of the excited activity of radium (measured by the β rays) for a long exposure to the emanation could be empirically expressed by the differences of two exponentials. The first definite statement of the changes occurring in the active deposit of radium and the existence of a rayless change occurs in a paper by RUTHERFORD and BARNES, 'Phil. Mag.,' Feb., 1904. A discussion of the evidence in which these conclusions were based was reserved for a later paper. A brief account of the theory of successive changes and the evidence of the existence of a rayless change in both radium and thorium was given in 'Radioactivity,' pp. 268–274. Somewhat later CURIE and DANNE ('Comptes Rendus,' 138, p. 683, 1904), using the hypothesis of successive changes advanced by RUTHERFORD and SODDY, arrived at a similar conclusion in regard to the changes in radium. In a later paper ('Comptes Rendus,' 138, p. 748, 1904), CURIE and DANNE gave an account of some important experiments on the effect of temperature on the curves of decay of activity, and showed that the product radium B could be separated from radium C by volatilization at a suitable temperature.

(2) A second 'rayless' change in which half the matter is transformed in 21 minutes;

(3) A third change in which half the matter is transformed in 28 minutes, and which gives rise to α, β, and γ rays.

9. *Theory of Successive Changes.*—Before considering the evidence from which these changes are deduced, the general theory of successive changes of radioactive matter will be considered. It is supposed that the matter A deposited by the emanation changes into B, B into C, C into D, and so on.

Each of these changes is supposed to take place according to the same law as a monomolecular change in chemistry, *i.e.*, the number N of particles unchanged after a time t is given by $N = N_0 e^{-\lambda t}$, where N_0 is the initial number and λ the constant of the change.

Since $dN/dt = -\lambda N$, the rate of change at any time is always proportional to the amount of matter unchanged. It has previously been pointed out that this law of decay of the activity of the radioactive products is an expression of the fact that the change is of the same type as a monomolecular chemical change.

Suppose that P, Q, R represent the number of particles of the matter A, B, and C respectively at any time t. Let λ_1, λ_2, λ_3 be the constants of change of the matter A, B, and C respectively.

Each atom of the matter A is supposed to give rise to one atom of the matter B, one atom of B to one of C, and so on.

The expelled 'rays' or particles are non-radioactive and so do not enter into the theory.

The general theory will first be considered corresponding to the practical cases of a very short and of a very long exposure in the presence of the emanation, then finally for any time of exposure to a constant supply of the emanation.

10. *Short Exposure.*—Suppose that a body has been exposed for a short interval in the presence of the radium or thorium emanation and then removed. The time is supposed to be so short that no appreciable portion of the deposited matter has undergone change during the time of exposure. It is required to find the number of particles P, Q, R of the matter A, B, C respectively present after any time t.

Then $P = ne^{-\lambda_1 t}$, if n is the number of particles that has been deposited during the short time of exposure. Now the increase of the number of particles dQ of the matter B per unit time is the number supplied by the change in the matter A, less the number due to the change of B into C, thus

$$dQ/dt = \lambda_1 P - \lambda_2 Q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

Similarly

$$dR/dt = \lambda_2 Q - \lambda_3 R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

Substituting in (1) the value of P in terms of n,

$$dQ/dt = \lambda_1 n e^{-\lambda_1 t} - \lambda_2 Q.$$

The solution of this equation is of the form

$$Q = n \left(a e^{-\lambda_1 t} + b e^{-\lambda_2 t} \right) \qquad \qquad (3).$$

By substitution it is found that $a = \lambda_1/(\lambda_2 - \lambda_1)$.

Since $Q = 0$ when $t = 0$, $b = -\lambda_1 (\lambda_2 - \lambda_1)$.
Thus

$$Q = \frac{n\lambda_1}{\lambda_1 - \lambda_2} \left(e^{-\lambda_2 t} - e^{-\lambda_1 t} \right) \qquad \qquad (4).$$

Substituting this value of Q in (2), it can readily be shown that

$$R = n \left(a e^{-\lambda_1 t} + b e^{-\lambda_2 t} + c e^{-\lambda_3 t} \right) \qquad \qquad (5),$$

where $a = \dfrac{\lambda_1 \lambda_2}{(\lambda_1 - \lambda_2)(\lambda_1 - \lambda_3)}$, $b = \dfrac{-\lambda_1 \lambda_2}{(\lambda_1 - \lambda_2)(\lambda_2 - \lambda_3)}$, $c = \dfrac{\lambda_1 \lambda_2}{(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)}$.

The variation of the values of P, Q, R with the time t after removal is shown graphically in fig. 8, curves A, B, and C respectively. In order to draw the curves
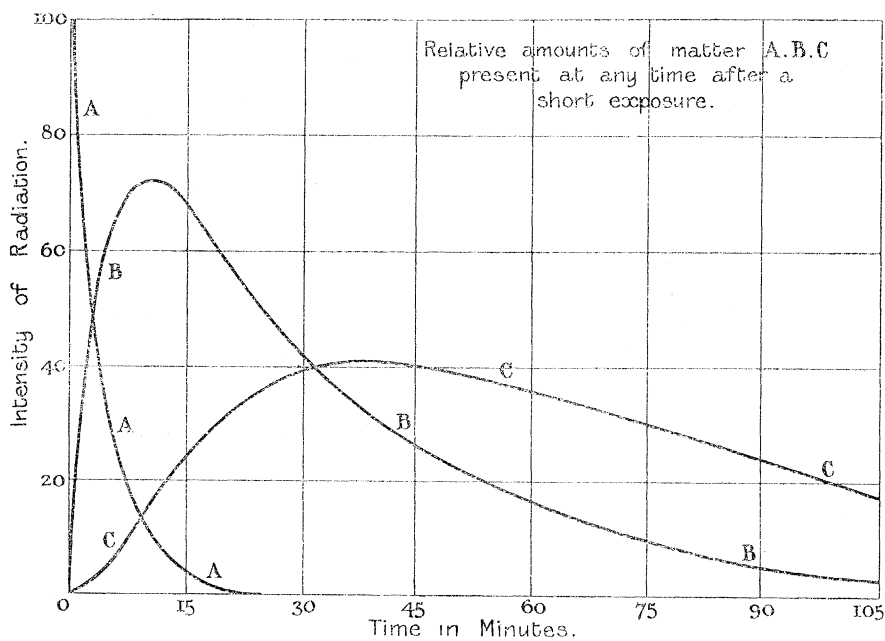
Fig. 8.

for the practical case corresponding to the first three changes in radium A, the values of λ_1, λ_2, λ_3 were taken as $3 \cdot 85 \times 10^{-3}$, $5 \cdot 38 \times 10^{-4}$, $4 \cdot 13 \times 10^{-4}$ respectively, *i.e.*, the times required for each type of matter to be half transformed are about 3, 21, and 28 minutes respectively.

The ordinates of the curves represent the relative number of atoms of the matter A, B, and C existing at any time, the value of n, the original number of atoms of the

matter A deposited, being taken as 100. The amount of matter B is initially zero, passes through a maximum about 10 minutes later, and then diminishes with the time. In a similar way, the amount of C passes through a maximum about 37 minutes after removal. After an interval of several hours the amount of both B and C diminishes very approximately according to an exponential law with the time, falling to half value after intervals of 21 and 28 minutes respectively.

11. *Long Exposure.*—The exposure is supposed to be so long that a state or equilibrium is reached between the emanation and the successive products resulting from it. In this case the number n_0 of particles of A, deposited per second from the emanation, is equal to the number of particles of A which change into B per second, and of B into C, and so on. This requires the relation

$$n_0 = \lambda_1 P_0 = \lambda_2 Q_0 = \lambda_3 R_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6),$$

where P_0, Q_0, R_0 are the maximum numbers of particles of the matter A, B, and C when a steady state is reached.

The values of P, Q, R at any time t after removal from a long exposure are given by equations of the same form as (3) and (5) for a short exposure. Remembering the condition that initially

$$P = P_0 = n_0/\lambda_1,$$

$$Q = Q_0 = n_0/\lambda_2,$$

$$R = R_0 = n_0/\lambda_3,$$

it can readily be shown that

$$P = \frac{n_0}{\lambda_1} e^{-\lambda_1 t} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7),$$

$$Q = \frac{n_0}{\lambda_1 - \lambda_2} \left(\frac{\lambda_1}{\lambda_2} e^{-\lambda_2 t} - e^{-\lambda_1 t} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8),$$

$$R = n_0 \left(a e^{-\lambda_1 t} + b e^{-\lambda_2 t} + c e^{-\lambda_3 t} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (9),$$

where

$$a = \frac{\lambda_2}{(\lambda_1 - \lambda_2)(\lambda_1 - \lambda_3)}, \quad b = \frac{-\lambda_1}{(\lambda_1 - \lambda_2)(\lambda_2 - \lambda_3)}, \quad c = \frac{\lambda_1 \lambda_2}{\lambda_3 (\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)}.$$

The relative numbers of atoms of P, Q, R existing at any time are shown graphically in fig. 9, curves A, B, and C respectively. The number of atoms R_0 is taken as 100 for comparison, and values of λ_1, λ_2, λ_3 are taken corresponding to the 3, 21, and 28-minute changes in the active deposit of radium. A comparison with fig. 8 for a short exposure brings out very clearly the variation in the relative amounts of P, Q, R in the two cases. The amount of R initially decreases very slowly. This is due to the fact that the supply of C due to breaking up of B at first, nearly compensates for the breaking up of C. The values of Q and R after several hours decrease exponentially, reaching half value every 28 minutes.
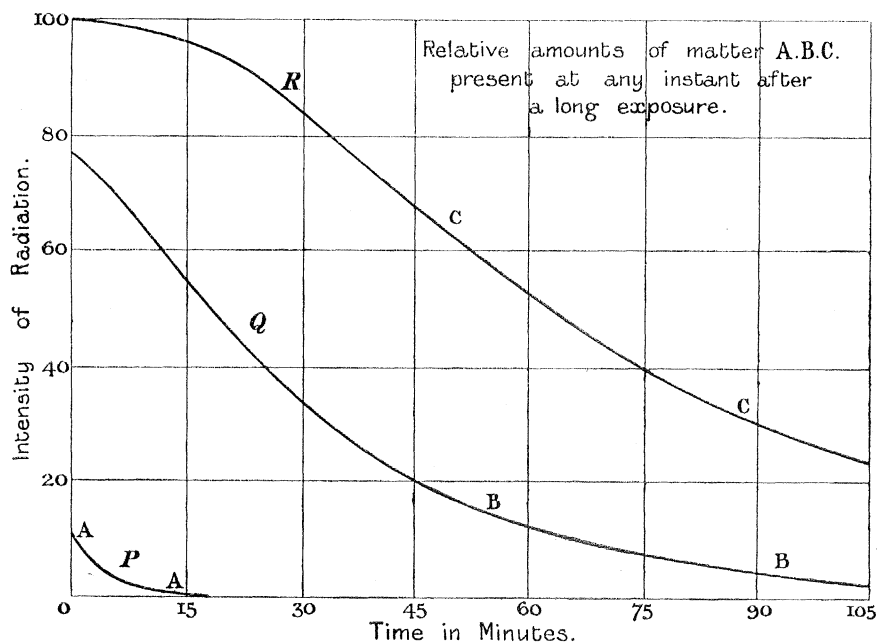
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Fig. 9.

12. *Any Time of Exposure.*—Suppose that a body is exposed in the presence of a constant supply of emanation, and that n_0 particles of the matter A are deposited each second. After a time of exposure T, the number of particles P_T of the matter A present is given by

$$P_T = n_0 \int_0^T e^{-\lambda_1 t}\, dt = \frac{n_0}{\lambda_1} (1 - e^{-\lambda_1 T}).$$

At any time t, after removal of the body from the emanation, the number of particles P of the matter A is given by

$$P = P_T e^{-\lambda_1 t} = \frac{n_0}{\lambda_1} (1 - e^{-\lambda_1 T}) e^{-\lambda_1 t}.$$

Consider the number of particles $n_0\, dt$ of the matter A deposited during the interval dt. At any time t later, the number of particles dQ of the matter B, which results from the change in A, is given (see equation 4) by

$$dQ = \frac{n_0 \lambda_1}{\lambda_1 - \lambda_2} (e^{-\lambda_2 t} - e^{-\lambda_1 t}) . \, dt . = n_0 f(t)\, dt \quad . \quad . \quad . \quad . \quad (10).$$

After a time of exposure T, the number of particles Q_T of the matter B present is readily seen to be given by

$$Q_T = n_0 \left[f(T)\, dt + f(T - dt)\, dt + \ldots \quad \ldots + f(0)\, dt \right]$$

$$= n_0 \int_0^T f(t)\, dt.$$

If the body is removed from the emanation after an exposure T, at any time t later the number of particles of B is in the same way given by

$$Q = n_0 \int_t^{T+t} f(t)\, dt.$$

It will be noted that the method of deduction of Q_T and Q is independent of the particular form of the function $f(t)$.

Substituting the particular value of $f(t)$ given in equation (10) and integrating, it can readily be deduced that

$$\frac{Q}{Q_T} = \frac{ae^{-\lambda_2 t} - be^{-\lambda_1 t}}{a - b} \qquad \dots \dots \dots \dots (11),$$

where

$$a = \frac{1 - e^{-\lambda_2 T}}{\lambda_2}, \quad b = \frac{1 - e^{-\lambda_1 T}}{\lambda_1}.$$

In a similar way, the number of particles R of the matter C present at any time can be deduced by substitution of the value of $f(t)$ in equation (5). These equations are, however, too complicated in form for simple application to experiment, and will be omitted.

13. *Changes in the Active Deposit from Thorium.*—If the variation of the activity, imparted to a body exposed for a short interval in the presence of the thorium emanation, is due to the fact that there are two successive changes in the deposited matter A, the first of which is a 'rayless' change, the activity I_t at any time t after removal should be proportional to the number Q_t of particles of the matter B present at that time. Now, from equation (4), it has been shown that

$$Q_t = \frac{\lambda_1 n}{\lambda_1 - \lambda_2}\left(e^{-\lambda_2 t} - e^{-\lambda_1 t}\right).$$

The value of Q_t passes through a maximum Q_T at the time T when

$$\lambda_2/\lambda_1 = e^{-(\lambda_1 - \lambda_2)\,T}.$$

The maximum activity I_T is proportional to Q_T and

$$\frac{I_t}{I_T} = \frac{Q_t}{Q_T} = \frac{e^{-\lambda_2 t} - e^{-\lambda_1 t}}{e^{-\lambda_2 T} - e^{-\lambda_1 T}} \qquad \dots \dots \dots \dots (12).$$

It will be shown later that the variation with time of the activity, imparted to a body by a short exposure, is expressed by an equation of the above form. It thus remains to fix the values of λ_1, λ_2. Since the above equation is symmetrical with regard to λ_1, λ_2, it is not possible to settle from the agreement of the theoretical and experimental curve which value of λ refers to the first change. The curve of variation of activity with time is unaltered if the values of λ_1 and λ_2 are interchanged.

It is found experimentally that the activity 5 or 6 hours after removal decays very approximately according to an exponential law with the time, falling to half value in 11 hours. This is the normal rate of decay of thorium for all time of exposure, provided measurements are not begun until several hours after the removal of the active body from the emanation.

This fixes the value of the constants of one of the changes. Let us assume for the moment that this gives the value of λ_1.

Then

$$\lambda_1 = 1{\cdot}75 \times 10^{-5}\,(\text{sec})^{-1}.$$

Since the maximum activity is reached after an interval $T = 220$ minutes (see fig. 1, curve C), substituting the values of λ_1 and T in equation (12), the value of λ_2 comes out to be

$$\lambda_2 = 2{\cdot}08 \times 10^{-4}\,(\text{sec})^{-1}.$$

This value of λ_2 corresponds to a change in which half the matter is transformed in 55 minutes.

Substituting now the values of λ_1, λ_2, T, the equation (12) reduces to

$$I_t/I_T = 1{\cdot}37\,(e^{-\lambda_2 t} - e^{-\lambda_1 t}).$$

The agreement between the results of the theoretical equation and the observed values is shown in the following table :—

Time in minutes.	Theoretical value of I_t/I_T.	Observed value of I_t/I_T.
15	·22	·23
30	·38	·37
60	·64	·63
120	·90	·91
220	1·00	1·00
305	·97	·96

It is thus seen that the curve of rise of activity for a short exposure is explained very satisfactorily on the supposition that two changes occur in the deposited matter, of which the first is a rayless change.

Further data are required in order to fix which of the time constants of the changes refers to the first change. In order to settle this point, it is necessary to isolate one of the products of the changes and to examine the variation of its activity with time. If, for example, a product can be separated whose activity decays to half value in 55 minutes, it would show that the second change is the more rapid of the two. Now PEGRAM* has examined the radioactive products obtained by electrolysis of

* 'Phys. Rev.,' p. 424, December, 1903.

thorium solutions. The rates of decay of the active products depended upon conditions, but he found that, in several cases, rapidly decaying products were obtained whose activity fell to half value in about 1 hour. Allowing for the probability that the product examined was not completely isolated by the electrolysis, but contained also a trace of the other product, this result would indicate that the last change which gives rise to rays is the more rapid of the two.

The results obtained by VON LERCH* in the electrolysis of solution of the active deposit also admit of a similar interpretation. Products were obtained on the electrodes of different rates of decay, but which lost half their activity in times varying from about 1 hour to 5 hours. This variation is possibly due to the admixture of the two products, but further experiment is necessary to settle this point with certainty. The evidence, as a whole, thus supports the conclusion that the active deposit from thorium undergoes two successive transformations as follows :—

(1) A 'rayless' change for which $\lambda_1 = 1\cdot 75 \times 10^{-5}$, *i.e.*, in which half the matter is transformed in 11 hours ;

(2) A second change giving rise to α, β and γ rays, for which $\lambda_2 = 2\cdot 08 \times 10^{-4}$, *i.e.*, in which half the matter is transformed in 55 minutes.†

It is, at first sight, a somewhat unexpected result that the final rate of decay of the active deposit from thorium does not in reality give the rate of change of the last product itself, but of the preceding product, which does not give rise to rays at all.

A similar peculiarity is observed in the decay of the excited activity of actinium, which is discussed in section 15.

14. For a long exposure in the presence of a constant supply of thorium emanation, the equation expressing the variation of activity with time is found from equation (8), section 11.

$$\frac{I_t}{I_0} = \frac{Q}{Q_0} = \frac{\lambda_2}{\lambda_2 - \lambda_1} e^{-\lambda_1 t} - \frac{\lambda_1}{\lambda_1 - \lambda_2} e^{-\lambda_2 t}$$

$$= \frac{\lambda_2 e^{-\lambda_1 t}}{\lambda_2 - \lambda_1} (1 - \cdot 083\, e^{-1\cdot 90 \times 10^{-4} t}).$$

About 4 hours after removal, the second term in the brackets becomes very small, and the activity after that time will decay very nearly according to an exponential law with the time, falling to half value in 11 hours. For any time of exposure T, the activity at time t after the removal (see equation 11) is given by

$$\frac{I_t}{I_0} = \frac{Q}{Q_T} = \frac{a e^{-\lambda_2 t} - b e^{-\lambda_1 t}}{a - b},$$

* 'Ann. d. Physik,' November, 1903.

† The 'rayless change' certainly does not give out α rays, and special experiments showed that no appreciable amount of β rays were present. On the other hand, the second change gives out all three types of rays.

where I_0 is the initial value of the activity, immediately after removal, and

$$a = \frac{1 - e^{-\lambda_2 T}}{\lambda_2}, \quad b = \frac{1 - e^{-\lambda_1 T}}{\lambda_1}.$$

By variation of T the curves of variation of activity for any time of exposure can be accurately deduced from the equation, when the values of the two constants λ_1, λ_2 are substituted. Miss BROOKS has examined the decay curves of excited activity for thorium for different times of exposure and has observed a substantial agreement between experiment and theory.*

15. *Changes in Actinium.*—Dr. GIESEL kindly forwarded me a radioactive preparation from pitchblende and called by him the 'emanating substance,' on account of the large amount of emanation it gives out. This had an activity, measured in the usual way, of about 250 times that of uranium. The emanation and excited activity produced by it were kindly examined for me in detail by Miss BROOKS. The emanation was found to have a very rapid rate of decay, its activity falling to half value in a few seconds. The excited activity for a long exposure fell to half value in 41 minutes. DEBIERNE† has shown that actinium gives off an emanation which loses half its activity in 3·7 seconds and produces excited activity which falls to half value in 41 minutes. There can be no doubt that the 'emanating substance' of GIESEL and the actinium of DEBIERNE contain the same radioactive constituent. The name actinium will thus be used in this paper to denote the 'emanating substance' of GIESEL. Miss BROOKS investigated the rate of decay of the excited activity of actinium for different times of exposure; but, for the purpose of elucidation of the changes occurring, we need only consider the curves of decay of excited activity for a short and for a long exposure. For a long exposure the activity decays very nearly according to an exponential law, falling to half value in 41 minutes. The value of the change-constant λ is $2·80 \times 10^{-4}$ $(\sec)^{-1}$.

The activity for a short exposure at first increases, rapidly passes through a maximum, and after some time decays according to an exponential law, falling to half value in 41 minutes. The curve of decay (measured by the α rays) for an exposure of 1·5 minutes in the presence of the actinium emanation is shown in fig. 10.

The maximum is reached about 7·5 minutes, reckoning from the moment the body is exposed to the emanation.

The curve is very similar in general shape to the corresponding curve of thorium, and can be analysed in a similar way; the activity at any time t is proportional to $e^{-\lambda_2 t} - e^{-\lambda_1 t}$.

These results show that the first change occurring in the active deposit from actinium is a rayless change. Since the activity finally decays according to an exponential law (half value in 41 minutes), one of the constants of the change has a value $2·80 \times 10^{-4}$.

[* 'Phil. Mag.,' September, 1904.]
† 'Comptes Rendus,' 138, p. 411, 1904.

By substitution in the curve, the value of the other constant is found to be $7 \cdot 7 \times 10^{-3}$ (half transformed in $1 \cdot 5$ minutes).

As in the case of thorium, a difficulty arises as to which value of λ applies to the rayless change, but the question in the case of actinium can at once be settled by means of electrolysis.
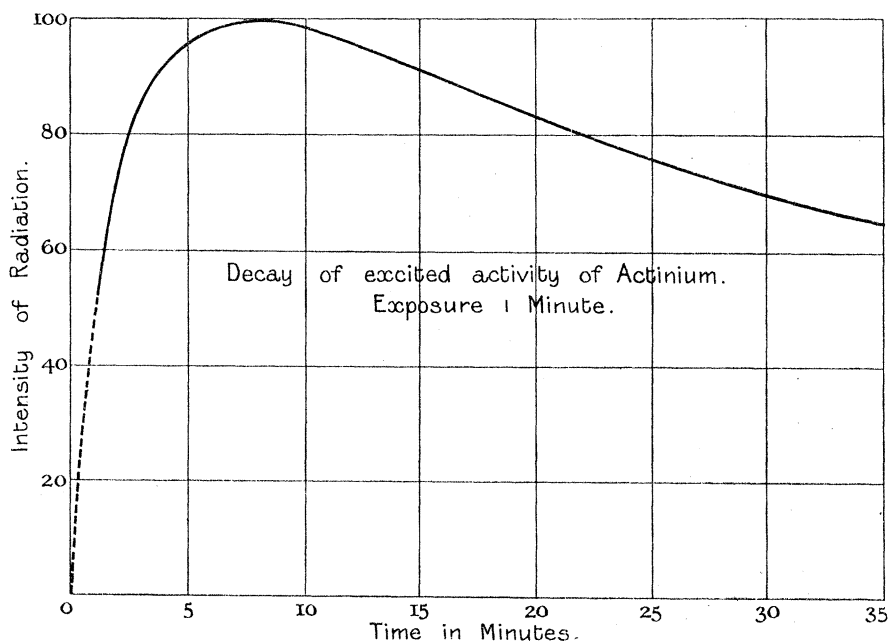

Fig. 10.

Miss Brooks performed the following experiment :—A platinum plate was made active in the presence of actinium and the active matter was dissolved off by hydrochloric acid and then electrolysed. The activity of the anode, after removal, fell very rapidly according to an exponential law, reaching half value in $1 \cdot 5$ minutes. The corresponding value of λ is $7 \cdot 7 \times 10^{-3}$. There is thus no doubt that the second change is the most rapid of the two. We may thus conclude that the active deposit from actinium undergoes two distinct successive transformations :

(1) A rayless change, in which half the matter is transformed in 41 minutes ;

(2) A change giving rise to α rays, in which half the matter is transformed in $1 \cdot 5$ minutes.*

It can readily be shown that, for a very short exposure of a body in the presence of the actinium emanation, the activity I_t at any time t is given by

$$I_t/I_T = 1 \cdot 14 \left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right),$$

where I_T is the maximum value of I which occurs at time $T = 7 \cdot 5$ minutes.

* The radiations from the products have not yet been examined to see whether β and γ rays are present.

For a very long exposure

$$I_t/I_0 = 1{\cdot}038\, e^{-\lambda_1 t} - {\cdot}038\, e^{-\lambda_2 t},$$

where I_0 is the initial value after removal, and

$$\lambda_1 = 2{\cdot}80 \times 10^{-4}, \quad \lambda_2 = 7{\cdot}7 \times 10^{-3}.$$

For the first 10 minutes after removal, the activity in consequence decays more slowly than is to be expected on a simple exponential law. This result has been observed experimentally. The variation of the activity for any time of exposure to the emanation is expressed by an equation of the same form as for thorium, equation (12), with the values λ_1, λ_2 found above.

There is some evidence that there is a product actinium X in actinium, corresponding to thorium X in thorium. This point is at present under investigation, and the results will be given in a later paper. If this is the case, actinium and thorium are very closely allied in the number and nature of their products. Both give rise to an emanation, and this is transformed into an active deposit which undergoes two further transformations, the first change being a 'rayless' one.

16. *Changes in the Active Deposit from Radium.*—In the case of the active deposit from radium, we are dealing with matter that undergoes at least four successive changes. For convenience, the matter initially produced from the emanation will be called the matter A and the succeeding products B, C, D, E respectively. The equations expressing the quantities of A, B, C, D present at any time are complicated, but the comparison of theory with experiment may be simplified by temporarily disregarding some unimportant terms. For example, the activity of the matter D is generally negligible compared with that of A or C, being as a rule less than 1/100,000 of the initial activity observed for the matter A or C. A still further simplification can be made by disregarding the first 3-minute change. In the course of 6 minutes after removal, three-quarters of the matter A has been transformed into B, and 20 minutes after removal all but about 1 per cent. has been transformed. The variation of the amount of matter B or C present at any time agrees more closely with the theory, if the first change is disregarded altogether. A discussion of this important point is given later in section 21.

17. *β-Ray Curves.*—The explanation of the β-ray curves (see figs. 5 and 6), obtained for different times of exposure, will be first considered. For a very short exposure, the activity measured by the β rays is small at first, passes through a maximum about 36 minutes later, and then decays steadily with the time.

The curve shown in fig. 6 is very similar in general shape to the corresponding thorium and actinium curves. It is thus necessary to suppose that the change of the matter B into C does not give rise to β rays, while the change of C into D does. In such a case the activity (measured by the β rays) is proportional to the amount of C present. Disregarding the first rapid change, the activity I_t at any time t should be

given by an equation of the same form (see equation 12, section 13) as for thorium and actinium, viz.,

$$\frac{I_t}{I_T} = \frac{e^{-\lambda_3 t} - e^{-\lambda_2 t}}{e^{-\lambda_3 T} - e^{-\lambda_2 T}},$$

where I_T is the maximum activity observed, which is reached after an interval T. Since the activity finally decays according to an exponential law (half value in 28 minutes), one of the values of λ is equal to $4 \cdot 13 \times 10^{-4}$. As in the case of thorium and actinium, the experimental curves do not allow us to settle whether this value of λ is to be given to λ_2 or λ_3. From other data (see section 20) it will be shown later that it must refer to λ_3. Thus $\lambda_3 = 4 \cdot 13 \times 10^{-4}$ (sec)$^{-1}$.

The experimental curve agrees very closely with theory if $\lambda_2 = 3 \cdot 10 \times 10^{-4}$ (sec)$^{-1}$.

The agreement between theory and experiment is shown by the table given below. The maximum value I_T (which is taken as 100) is reached at a time $T = 36$ minutes.

In order to obtain the β-ray curve, the following procedure was adopted. A layer of thin aluminium was placed inside a glass tube, which was then exhausted. A large quantity of radium emanation was then suddenly introduced by opening a stopcock communicating with the emanation vessel, which was at atmospheric pressure. The emanation was left in the tube for $1 \cdot 5$ minutes and then was rapidly swept out by a current of air. The aluminium was then removed and was placed under an electroscope, such as is shown in fig. 3. The α rays from the aluminium were cut off by an interposed screen of aluminium $\cdot 1$ millim. thick. The time was reckoned from a period of 45 seconds after the introduction of the emanation.

Time in minutes.	Theoretical value of activity.	Observed value of activity.
0	0	0
10	58·1	55
20	88·6	86
30	97·3	97
36	100	100
40	99·8	99·5
50	93·4	92
60	83·4	82
80	63·7	61·5
100	44·8	42·5
120	30·8	29

There is thus a fairly good agreement between the calculated and observed values of the activity measured by the β rays.

The results are thus satisfactorily explained if it is supposed :—

(1) That the change B into C (half transformed in 21 minutes) does not give rise to β rays ;

(2) That the change C into D (half transformed in 28 minutes) gives rise to β rays.

These conclusions are very strongly supported by observations of the decay measured by the β rays for a long exposure. The curve of decay is shown in fig. 6 and fig. 11, curve I.
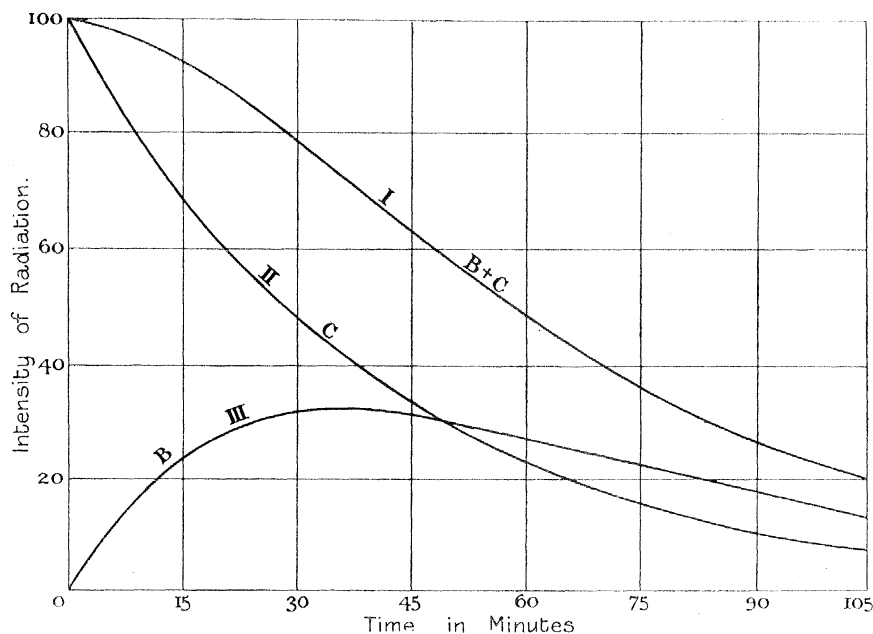

Fig. 11.

P. CURIE and DANNE made the important observation that the curve of decay C, shown in fig. 7, for a long exposure, could be accurately expressed by an empirical equation of the form

$$I_t/I_0 = ae^{-\lambda_3 t} - (a - 1)\,e^{-\lambda_2 t},$$

where $\lambda_2 = 3\cdot10 \times 10^{-4}\,(\mathrm{sec})^{-1}$ and $\lambda_3 = 4\cdot13 \times 10^{-4}\,(\mathrm{sec})^{-1}$, and $a = 4\cdot20$ is a numerical constant.

I have found that within the limit of experimental error this equation represents the decay of excited activity of radium for a long exposure, measured by the β rays. The equation expressing the decay of activity, measured by the α rays, differs considerably from this, especially in the early part of the curve. Several hours after removal the activity decays according to an exponential law with the time, decreasing to half value in 28 minutes. This fixes the value of λ_3. The constant a and the value of λ_2 are deduced from the experimental curve by trial. Now we have already shown (section 14) that in the case of the active deposit from thorium, where there are two changes of constants λ_2 and λ_3, in which only the second change gives rise to a radiation, the value of

$$\frac{I_t}{I_0} = \frac{\lambda_2}{\lambda_2 - \lambda_3}\,e^{-\lambda_3 t} - \frac{\lambda_3}{\lambda_2 - \lambda_3}\,e^{-\lambda_2 t}$$

for a long time of exposure (see equation 8). This is an equation of the same form

as that found experimentally by Curie and Danne. On substituting the values λ_2, λ_3 found by them,

$$\frac{\lambda_2}{\lambda_2 - \lambda_3} = 4\cdot3, \quad \text{and} \quad \frac{\lambda_1}{\lambda_1 - \lambda_3} = 3\cdot3.$$

Thus not only does the theoretical equation agree in form, but also closely in the values of the numerical constants. If the first as well as the second change gave rise to a radiation, the equation would be of the same general form, but the value of the numerical constants would be different, the values depending upon the ratio of the ionization in the first and second changes. If, for example, it is supposed that both changes give out β rays in equal amounts, it can readily be calculated that the equation of decay would be

$$\frac{I_t}{I_0} = \frac{\cdot5\lambda_2}{\lambda_2 - \lambda_3} e^{-\lambda_3 t} - \cdot5 \left(\frac{\lambda_3}{\lambda_2 - \lambda_3} - 1 \right) e^{-\lambda_2 t}.$$

Taking the values of λ_2 and λ_3 found by Curie, the numerical factor $e^{-\lambda_3 t}$ becomes $2\cdot15$ instead of $4\cdot3$ and $1\cdot15$ instead of $3\cdot3$. The theoretical curve of decay in this case would be readily distinguishable from the observed curve of decay. The fact that the equation of decay found by Curie and Danne involves the necessity of an initial rayless change can be simply shown as follows:—

Curve I. (fig. 11) shows the experimental curve. At the moment of removal of the body from the emanation (disregarding the initial rapid change), the matter must consist of both B and C. Consider the matter which existed in the form C at the moment of removal. It will be transformed according to an exponential law, the activity falling to half in 28 minutes. This is shown in curve II. Curve III. represents the difference between the ordinates of curves I. and II. It will be seen that it is identical in shape with the curve (fig. 5) showing the variation of the activity for a short exposure, measured by the β rays. It passes through a maximum at the same time (about 36 minutes). The explanation of such a curve is only possible on the assumption that the first change is a rayless one. The ordinates of curve III. express the activity added in consequence of the change of the matter B, present after removal, into the matter C. The matter B present gradually changes into C, and this, in its change to D, gives rise to the radiation observed. Since the matter B alone is considered, the variation of activity with time due to its further changes, shown by curve III., should agree with the curve obtained for a short exposure (see fig. 5), and this, as we have seen, is the case.

The agreement between theory and experiment is shown in the following tables. The first column gives the theoretical curve of decay for a long exposure deduced from the equation

$$\frac{I_t}{I_0} = \frac{\lambda_2}{\lambda_2 - \lambda_3} e^{-\lambda_3 t} - \frac{\lambda_3}{\lambda_2 - \lambda_3} e^{-\lambda_2 t},$$

taking the value of $\lambda_2 = 3\cdot10 \times 10^{-4}$ and $\lambda_3 = 4\cdot13 \times 10^{-4}$.

The second column gives the observed activity (measured by means of an electroscope) for a long exposure of 24 hours in the presence of the emanation.

Time in minutes.	Calculated values.	Observed values.
0	100	100
10	96·8	97·0
20	89·4	88·5
30	78·6	77·5
40	69·2	67·5
50	59·9	57·0
60	49·2	48·2
80	34·2	33·5
100	22·7	22·5
120	14·9	14·5

In cases where a steady current of air is drawn over the active body, the observed values are slightly lower than the theoretical. This is probably due to a slight volatility of the product radium B at ordinary temperatures.

18. *α-Ray Curves.*—The analysis of the decay curves of the excited activity of radium, measured by the α rays, will now be discussed. The following table shows the variation of the intensity of the radiation after a long exposure in the presence of the
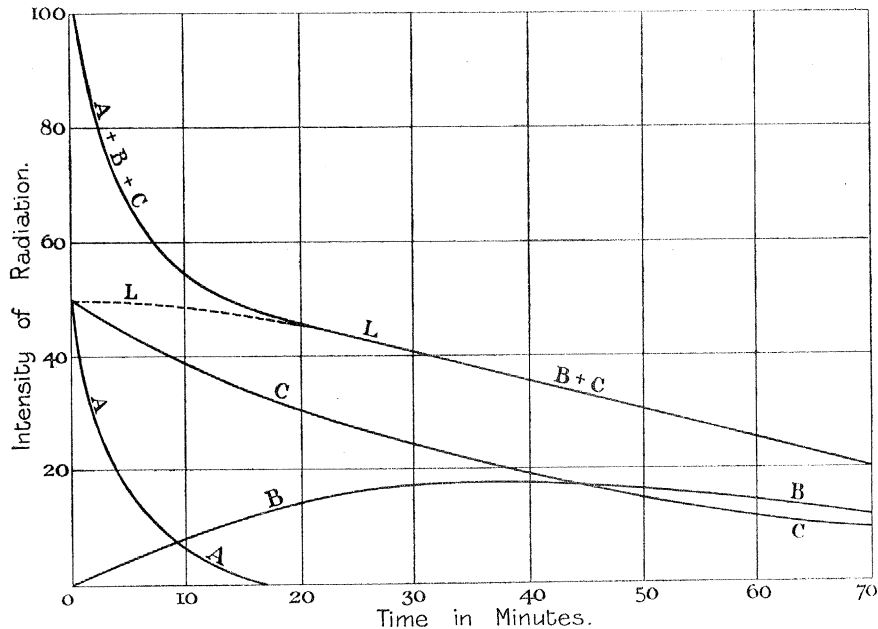

Fig. 12.

radium emanation. A platinum plate was made active by exposure of several days in a glass tube containing a large quantity of emanation. The active platinum after removal was placed on the lower of two parallel insulated lead plates, and a saturating electromotive force of 600 volts was applied. The ionization current was sufficiently

large to be measured by means of a sensitive high-resistance galvanometer, and readings were taken as quickly as possible after removal of the platinum from the emanation vessel. The initial value of the current (taken as 100) was deduced by continuing the curves backwards to meet the vertical axis (see fig. 12), and was found to be 3×10^{-8} ampère.

Time in minutes.	Current.	Time in minutes.	Current.
0	100	30	40·4
2	80	40	35·6
4	69·5	50	30·4
6	62·4	60	25·4
8	57·6	80	17·4
10	52·0	100	11·6
15	48·4	120	7·6
20	45·4		

These results are shown graphically in the upper curve of fig. 12. The initial rapid decrease is due to the decay of the activity of the matter A. If the slope of the curve is produced backwards from a time 20 minutes after removal, it cuts the vertical axis at about 50. The difference between the ordinates of the curves A+B+C and LL at any time is shown in the curve AA. The curve AA represents the activity at any time supplied by the change in radium A. The curve LL starting from the vertical axis is identical with the curve already considered, representing the decay of activity measured by the β rays for a long exposure (see fig. 6). This is shown by the agreement of the numbers in the following tables. The first column in the table below gives the theoretical values of the activity deduced from the equation

$$\frac{I_t}{I_0} = \frac{\lambda_2}{\lambda_2 - \lambda_3} e^{-\lambda_3 t} - \frac{\lambda_3}{\lambda_2 - \lambda_3} e^{-\lambda_2 t}$$

for the values of λ_2, λ_3 previously employed. The second column gives the observed values of the activity deduced from the decay curve LL.

Time in minutes.	Calculated value of activity.	Observed value of activity.
0	100	100
10	96·8	97·0
20	89·4	89·2
30	78·6	80·8
40	69·2	71·2
50	59·9	60·8
60	49·2	50·1
80	34·2	34·8
100	22·7	23·2
120	14·9	15·2

The close agreement of the curve LL with the theoretical curve deduced on the assumption that there are two changes, the first of which does not emit rays, shows that the change of radium B into C does not emit α rays. In a similar way, as in the curve I, fig. 11, the curve LL may be analysed into its two components represented by the two curves CC and BB. The curve CC represents the activity supplied by the matter C present at the moment of removal. The curve BB represents the activity resulting from the change B into C and is identical with the corresponding curve in fig. 11. Using the same line of reasoning as before, we may thus conclude that the change of B into C is not accompanied by α rays. It has already been shown that it does not give rise to β rays, and the identity of the β and γ-ray curves show that it does not give rise to γ rays. The change B into C is thus a 'rayless' change, while the change C into D gives rise to all three kinds of rays.

An analysis of the decay of the excited activity of radium thus shows that three distinct rapid changes occur in the deposited matter, viz. :—

(1) The matter A, derived from the change in the emanation, is half transformed in 3 minutes and is accompanied by α rays alone ;

(2) The matter B is half transformed in 21 minutes and gives rise to no ionizing rays ;

(3) The matter C is half transformed in 28 minutes and is accompanied by α, β and γ rays ;

(4) A fourth very slow change, which will be discussed later (section 23).

19. *Equations Representing the Activity Curves.*—The equations representing the variation of activity with time are for convenience collected below, where $\lambda_1 = 3\cdot8 \times 10^{-3}$, $\lambda_2 = 3\cdot10 \times 10^{-4}$, $\lambda_3 = 4\cdot13 \times 10^{-4}$:—

(1) Short exposure : activity measured by β rays,

$$I_t/I_T = 10\cdot3 \left(e^{-\lambda_3 t} - e^{-\lambda_2 t}\right),$$

where I_T is the maximum value of the activity ;

(2) Long exposure : activity measured by β rays,

$$I_t/I_0 = 4\cdot3 \, e^{-\lambda_3 t} - 3\cdot3 \, e^{-\lambda_2 t},$$

where I_0 is the initial value ;

(3) Any time of exposure T : activity measured by the β rays,

$$\frac{I_t}{I_0} = \frac{ae^{-\lambda_3 t} - be^{-\lambda_2 t}}{a - b},$$

where

$$a = \frac{1 - e^{-\lambda_3 T}}{\lambda_3}, \qquad b = \frac{1 - e^{-\lambda_2 T}}{\lambda_2} ;$$

(4) Activity measured by α rays : long time of exposure,

$$\frac{I_t}{I_0} = \tfrac{1}{2} e^{-\lambda_1 t} + \tfrac{1}{2} \left(4\cdot3 \, e^{-\lambda_3 t} - 3\cdot3 \, e^{-\lambda_2 t}\right).$$

The equations for the α rays for any time of exposure can be readily deduced, but the expressions are somewhat complicated.

20. *Equations of Rise of Excited Activity.*—The curves expressing the gradual increase to a maximum of the excited activity produced on a body exposed in the presence of a constant amount of emanation are complementary to the curves of decay for a long exposure. The sum of the ordinates of the rise and decay curves is at any time a constant. This necessarily follows from the theory and can also be simply deduced from *à priori* considerations. ('Radioactivity,' p. 267.)

The curves of rise and decay of the excited activity are shown graphically in fig. 13 for both the α and β rays. The thick line curves are for the α rays. The
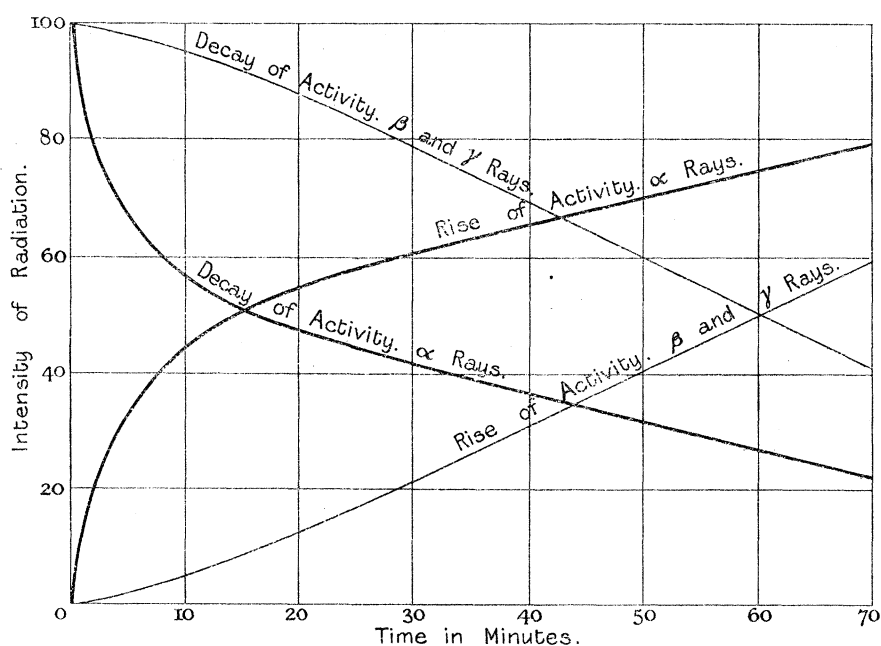

Fig. 13.

difference between the shapes of the decay curves when measured by the α or β rays is clearly brought out in the figure. The equations representing the rise of activity to a maximum are given below.

For the β and γ rays,

$$I_t/I_{max} = 1 - \left(4 \cdot 3\, e^{-\lambda_3 t} - 3 \cdot 3\, e^{-\lambda_2 t}\right).$$

For the α rays,

$$I_t/I_{max} = 1 - \tfrac{1}{2}\, e^{-\lambda_1 t} - \tfrac{1}{2}\left(4 \cdot 3\, e^{-\lambda_3 t} - 3 \cdot 3\, e^{-\lambda_2 t}\right).$$

21. *Effect of Temperature.*—We have so far not considered the evidence on which the 28-minute rather than 21-minute change is supposed to take place in the matter C. This evidence has been supplied by some recent important experiments of P. CURIE and DANNE* on the volatilization of the active matter deposited by the emanation.

* 'Comptes Rendus,' 138, p. 748, 1904.

Miss GATES* showed that this active matter was volatilized from a platinum wire above a red heat and deposited on the surface of a cold cylinder surrounding the wire. CURIE and DANNE extended these results by subjecting an active platinum wire *for a short time* to the action of temperatures varying between 15° C. and 1350° C., and then examining at room temperatures the decay curves not only for the active matter remaining on the wire, but also for the volatilized part. They found that the activity of the distilled part always increased after removal, passed through a maximum, and finally decayed according to an exponential law (half value in 28 minutes). At a temperature of about 630° C. the active matter left behind on the wire decayed at once according to an exponential law, falling to half value in 28 minutes. P. CURIE and DANNE showed that the matter B is much more volatile than C. The former is completely volatilized at about 600° C., while the latter is not completely volatilized even at a temperature of 1300° C. The fact that the matter C, left behind when B is completely volatilized, decays at once to half value in 28 minutes shows that the matter C itself and not B is half transformed in 28 minutes.

CURIE and DANNE also found that the rate of decay of the active matter varied with the temperature to which the platinum wire had been subjected. At 630° C. the rate of decay was normal, at 1100° C. the activity fell to half value in about 20 minutes, while at 1300° C. it fell to about half value in about 25 minutes.

I have repeated the experiments of CURIE and DANNE and obtained very similar results. It was thought possible that the measured rate of decay observed after heating might be due to a permanent increase in the rate of volatilization of C at ordinary temperatures. This explanation, however, is not tenable, for it was found that the activity decreased at the same rate whether the activity of the wire was tested in a closed tube or in the open with a current of air passed over it.

These results are of great importance, for they indicate that the rate of change of the product C is not a constant, but is affected by differences of temperature. This is the first case where temperature has been shown to exert an appreciable influence on the rate of change of any radioactive product.

22. *Effect of the First Rapid Change.*—We have seen that the law of decay of activity, measured by the β or γ rays, can be very satisfactorily explained if the first 3-minute change is disregarded. The full theoretical examination of the question given in sections 10 and 11 and the curves of figs. 8 and 9 shows, however, that the presence of the first change should exercise an effect of sufficient magnitude to be detected in measurements of the activity due to the succeeding changes. The question is of great interest, for it involves the important theoretical point whether the substances A and B are produced independently of one another, or whether A is the parent of B. In the latter case, the matter A which is present changes into B,

* 'Phys. Rev.,' p. 300, 1903.

and, in consequence, the amount of B present after A is transformed should be somewhat greater than if B were produced independently. Since the change of A is fairly rapid, the effect should be most marked in the early part of the curve.

In order to examine this point experimentally, the curve of rise of activity, measured by the β rays, was determined immediately after the introduction of a large quantity of the radium emanation into a closed vessel. The curve of decay of activity on a body after removal of the emanation, and the rise of activity after the introduction of the emanation, are in all cases complementary to one another. While, however, it is difficult to measure with certainty whether the activity has fallen in a given time, for example, from 100 to 99 or 98·5, it is easy to be sure whether the corresponding rise of activity in the converse experiment is 1 or 1·5 per cent. of the final amount. Fig. 14, curve I., shows the rise of activity (measured by the β rays)
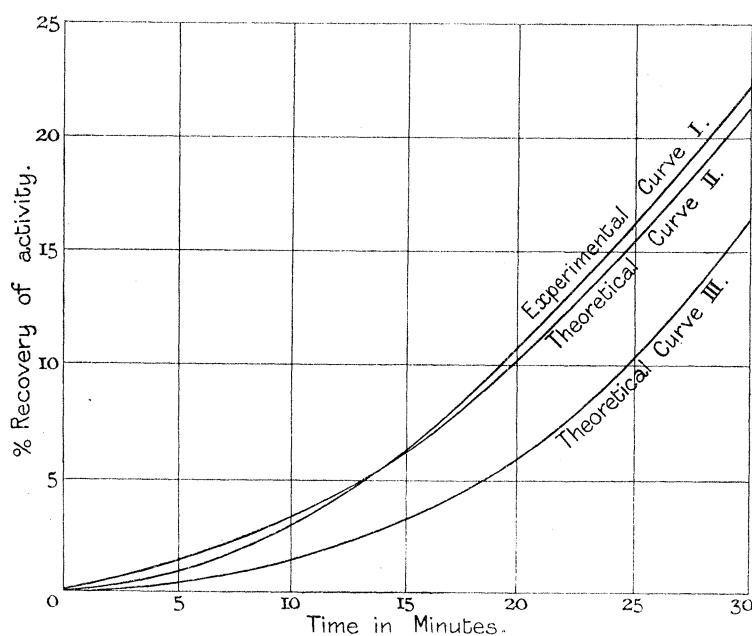

Fig. 14.

obtained for an interval of 20 minutes after the introduction of the emanation. The ordinates represent the percentage amount of the final activity regained at any time.

Curve III. shows the theoretical curve obtained on the assumption that A is a parent of B. This curve is calculated from equation (9) discussed in section 11, and λ_1, λ_2, λ_3 are the values previously found.

Curve II. gives the theoretical activity at any time on the assumption that the substances A and B arise independently. This is calculated from an equation of the same form as (8).

It is seen that the experimental results agree best with the view that A and B arise independently. Such a conclusion, however, is of too great importance to be accepted before examining closely whether the theoretical conditions are fulfilled in

the experiments. In the first place, it is assumed that the carriers which give rise to excited activity are deposited on the surface of the body, to be made active immediately after their formation. There is some evidence, however, that some of these carriers exist for a considerable interval in the gas before their deposit on the body. For example, it is found that if a body is introduced for a short interval, about 1 minute, into a vessel containing the radium emanation, which has remained undisturbed for several hours, the activity after the first rapid decay (see fig. 4, curve B) is in much greater proportion than if an electric field had been acting for some time previously. This result indicates that the carriers of B and C both collect in the gas and are swept to the electrode when an electric field is applied. This effect may in part be due to a slight volatility of the matter B at ordinary temperatures.* If the matter B exists to some extent in the gas, the difference between the theoretical curves for three successive changes would be explained; for, in transferring the emanation to another vessel, the matter B mixed with it would commence at once to change into C and give rise to a part of the radiation observed.

The equal division of the activity between the products A and C (see fig. 12) supports the view that C is a product of A, for when radioactive equilibrium is reached, the number of particles of A changing per second is equal to the number of B or C changing per second. If each atom of A and C expels an α particle of the same mass and with the same average velocity, the activity due to the matter A should be equal to that due to the matter C; and this, as we have seen, is the case. Further investigations are in progress, which it is hoped will throw more light on this difficult question.

23. *Very Slow Change in the Active Deposit from Radium.*—M. and Mme. CURIE† have observed that bodies which have been exposed for a long interval in the presence of the radium emanation do not lose all of their activity. The excited activity at first decays according to the equations already considered, but a residual activity always remains, of the order of 1/20,000 of the initial activity. This residual activity seemed fairly permanent, for it did not decay during an interval of six months. GIESEL observed that a platinum wire which has been exposed to the radium emanation shows residual activity, and he states that the radiation consists entirely of α rays.

I have examined this residual activity in the following way. The emanation from 30 milligs. of pure radium bromide was condensed in a small glass tube and the ends of the tube sealed. After standing for a month the tube was opened, and left to

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* This result is supported by some recent experiments of Miss BROOKS ('Nature,' July 21, 1904). It was shown that the matter B is volatile at ordinary temperatures, and a small part escapes from the active body and is deposited in the neighbourhood. It was also observed that the volatility of the matter B was far more marked during the first 10 minutes after removal, *i.e.*, during the time the first change is in progress. If A is the parent of B, the expulsion of a charged α particle must set B in motion, and in consequence some of the atoms of B may acquire sufficient velocity to escape from the active body.

† 'Thèse présentée à la Faculté des Sciences,' Paris, 1903, p. 116.

stand for several days, in order to allow all the remaining emanation to escape. The inside of the glass tube was found to show considerable activity. The tube was then filled with dilute sulphuric acid, and, after standing several hours, the acid was removed and evaporated down to dryness in a flat glass dish. Most of the active matter in the glass tube was dissolved out by the acid, and, after evaporation, a strongly active residue was obtained in the glass dish. The active matter was found to give out both α and β rays, and the β rays were present in a very unusual proportion; thus, compared with the intensity of the α rays, the β rays were present in at least 10 times greater proportion than for a thin layer of uranium, thorium, or radium, in a state of radioactive equilibrium.

The intensity of the α radiation was first tested when the active deposit was about 2 months old. The activity, at that time, did not vary apparently over a week's interval. Owing to a numerical error it was at first thought that the activity did not change during a further interval of 3 months; but the corrected result showed that the activity had more than doubled itself during that interval. Still later observations show that the α-ray activity is steadily increasing.

The increase of the α-ray activity with time has been confirmed by observations of the residual activity left behind on a platinum plate exposed to the emanation. The results then showed that the α-ray activity during the first month, after removal, increases considerably. The relative proportion of β to α rays steadily diminishes with the time. This is not due to a diminution of the β-ray activity, but to an increase of the α-ray activity. Further observations are in progress to examine the variations of the activity over long periods of time.

The results, so far as they have gone, show that the residual activity produced on bodies by exposure to the radium emanation is very complicated. The results discussed in the next section show that the large β-ray activity is due to matter of different chemical properties from that which gives rise to the α rays.

The increase of the α-ray activity with time indicates that the deposited matter undergoes a slow 'rayless' change. The evidence at present obtained points to the conclusion that the deposited matter is initially complex. A small portion of the total amount undergoes a change, accompanied by the emission of β rays alone. The main portion of the deposited matter undergoes a very slow 'rayless' transformation, and the resulting product or products give rise to α rays.

Observations extending over a long period of time will be required to determine the period of these changes. It seems probable that radium C breaks up into two distinct products. The major part of the product then undergoes a further change or succession of changes.*

* [*October* 10, 1904.—Further experimental work on this subject has led to a modification of the above conclusions. It has been found that the results are best explained on the supposition that radium C gives rise to radium D, which in breaking up emits only β (and probably γ) rays. Radium D produces radium E, which breaks up with the emission of only α rays. It has been deduced that D is probably half

24. *Connection of Slowly Decaying Product with Radio-Tellurium.*—Some evidence will now be considered which points to the strong probability that one of these slowly changing products of radium is the same as the active constituent present in radio-tellurium, separated from pitchblende by MARCKWALD.

It will be recalled that the polonium of Mme. CURIE is always obtained with bismuth, but can be partially separated from it by several distinct methods. GIESEL early observed that a bismuth plate dipped into a radium solution became permanently active and gave out only α rays, and in this respect resembled the polonium of Mme. CURIE.

GIESEL has throughout insisted that polonium was nothing more than 'induced bismuth'—apparently considering that the bismuth acquired the radioactive property by mixture with a radium solution. Taking the point of view that radioactivity is always the result of changes occurring in special kinds of matter, the experiments of GIESEL indicate that a radioactive product is deposited from the radium solution on to the bismuth plate, and that the activity of the plate is not due to the bismuth at all, but to radioactive matter deposited on its surface.

MARCKWALD found that a bismuth plate dipped into a solution of pitchblende was coated with a radioactive deposit. He at first thought this activity was due to the tellurium which was deposited on the plate, and consequently gave it the name radio-tellurium. Later results have, however, shown that the activity has nothing whatever to do with the tellurium, and by suitable chemical methods he has separated an extremely active substance. MARCKWALD states that the radio-tellurium gives out only α rays, and has not appreciably changed during six months after separation. Mme. CURIE found that the active constituent present in bismuth, which had been made active by placing it in a radium solution, could be fractionated in the same way as polonium, and in that way was able to obtain bismuth 2000 times as active as uranium, but this activity decreased with the time.

An account will now be given of some experiments to ascertain if there is any connection between this slowly decaying product of radium and radio-tellurium or polonium.

The active matter deposited on the glass tube, in which a large amount of radium emanation had been stored for a month, was dissolved in sulphuric acid. A bismuth plate was introduced into the solution and left for several hours. The bismuth plate was found to be strongly active and to give out only α rays. On adding a second bismuth plate, very little active matter was deposited upon it. The remaining solution was then evaporated, and the residue was found to be about as active as the bismuth plate, and to give out both α and β rays. There is thus no doubt that the matter dissolved off the glass is complex, and one part is deposited on bismuth and

transformed in 40 years and E in about 1 year. This modification has been introduced into the subsequent schedules in the text. A full account of these experiments was communicated to the Electrical Congress at St. Louis (September 16, 1904) in a paper entitled "Further Transformation Products of Radium."]

the other not. The activity of the bismuth plate did not appreciably change during a month's interval.* Part of the active matter obtained from the sulphuric acid solution then behaves in a similar way to the radio-tellurium of MARCKWALD, inasmuch as it gives out only α rays, and is readily deposited on bismuth. In order to test the apparent similarity still further, an accurate comparison was made between the penetrating power of the rays from the active bismuth and a bismuth plate of radio-tellurium obtained from Dr. STHAMER, of Hamburg. The rays were found initially to be about half absorbed in a thickness of ·00034 centim. of aluminium, and exhibited the characteristic property of the rays of rapidly increasing absorption with the thickness of matter traversed. No appreciable difference in the penetrating power of the α rays from the two substances was observed, although the intensity of the radiations was reduced to less than 1 per cent. of the initial value. It has been found experimentally that the rays from the different radioactive products differ in penetrating power, and the curve of absorption for different thicknesses of absorbing material is, in general, a characteristic of each product.

The identity of the curves of absorption of the α rays from the active bismuth and the radio-tellurium, coupled with the similarity of the radiations and chemical properties, is very strong evidence that the active product is in each case the same. I think there can be little doubt that the active constituent of radio-tellurium of MARCKWALD is a disintegration product of radium.

The polonium (radioactive bismuth) obtained by me from Paris loses its activity fairly rapidly, and the α rays from it are more readily absorbed than the α rays of radio-tellurium. This greater absorption may, however, be due in part to the fact that the radiations from the polonium come from the mass of the bismuth, and in consequence are made up of rays of widely different penetrating power, while the rays from the radio-tellurium arise from a thin film of matter deposited on the bismuth plate, in which the absorption of the issuing rays would be small. The identity or otherwise of the constituent present in the polonium of Mme. CURIE and the radio-tellurium of MARCKWALD has been a much vexed question. A definite answer cannot be given until accurate observations have been made of the change of activity with time of these products.

25. *Radioactivity observed in Ordinary Matter.*—A large number of experimenters have observed that ordinary matter possesses the property of radioactivity to a feeble degree. R. J. STRUTT found that different samples of the same metal showed wide differences in radioactive power. It is a matter of great importance to settle whether the weak radioactivity observed is a property of the substance under examination or is due to a minute radioactive impurity. I think there is little doubt that the radioactivity observed in some substances is due in part to a deposit of radioactive matter on its surface from the atmosphere. It has now been conclusively

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* This bismuth plate was unfortunately mislaid during my visit to England in May. I am, in consequence, unable to give a more definite statement in regard to the change of the activity with time.

shown that the radium emanation is present in the atmosphere. This, in the course of its disintegration, gives rise to the slowly decaying product, which will be deposited from the air on the surface of all bodies exposed in the open. Such bodies will thus be covered with an invisible film of radioactive matter of very slow rate of change. The results of COOKE* are a strong confirmation of this point of view. By carefully polishing the surface of a brass electroscope, he was able to reduce its rate of discharge to almost one-third of the normal amount. In such a case the radioactive matter was removed from the surface by the process of polishing. The strong radioactivity observed in a room in which radium preparations have once been used, is probably due to the deposit on the walls of the room of this slowly decaying matter from the emanation.

26. *Comparison of the Changes in the Radio-Elements.*—The changes occurring in the three radio-elements and the radiations which accompany them are shown graphically in fig. 15. The radiations from actinium have not yet been sufficiently
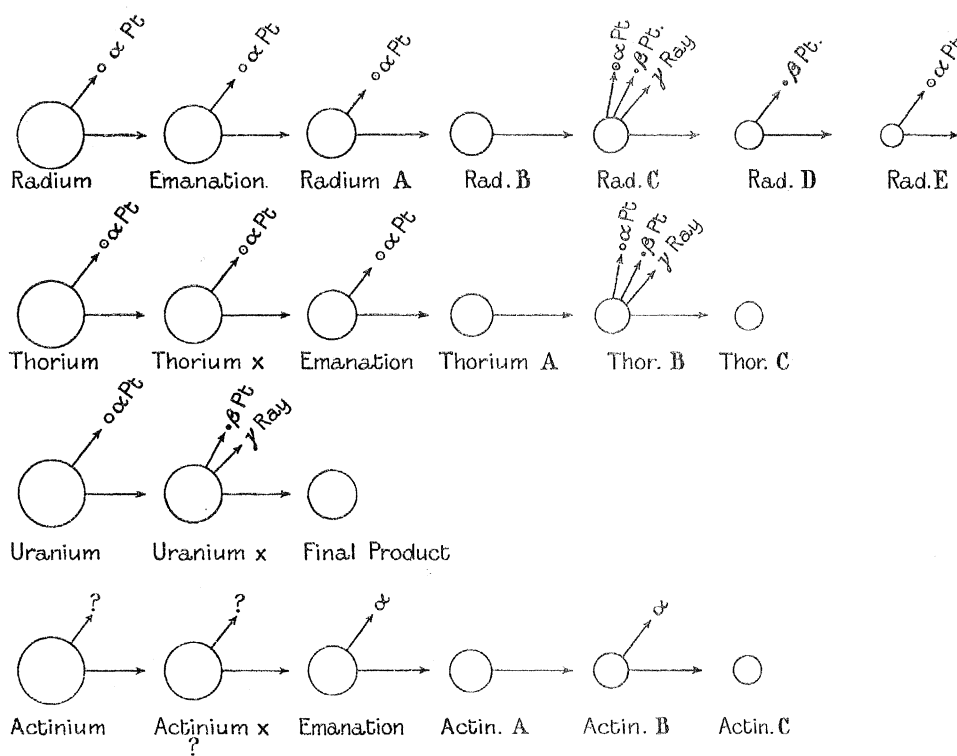

Fig. 15.

examined to be certain where the β or γ rays appear in the last change as in the case of thorium. It will be seen that there are, at least, six successive changes in radium, five in thorium, and two in uranium. The first five changes in radium are analogous, in many respects, to the corresponding changes in thorium and actinium. Each of

* 'Phil. Mag.,' August, 1903.

these elements gives rise to a gaseous product, the emanation, and this in turn is transformed into a type of matter which is deposited on the surface of bodies. In both thorium and radium, the fourth change is followed by a change in which all three types of rays appear together, while the third product in all three elements does not emit rays at all. The remarkable similarity in the nature of the changes occurring in radium, thorium, and actinium, indicates that the constitution of the atoms of these bodies is very similar.

The time T taken for each product to be half transformed, and the value of the related constant λ, the fractional amount of the product changed per second, are shown in the following table, together with some of the physical and chemical properties of the products :—

Product.	T.	λ (sec)$^{-1}$.	Some physical and chemical properties.
URANIUM $\downarrow$	10^9 years	$2\cdot2\times10^{-17}$	Soluble in excess of ammonium carbonate.
Uranium X $\downarrow$	22 days	$3\cdot6\times10^{-7}$	Insoluble in excess of ammonium carbonate.
Final product.	—	—	
THORIUM $\downarrow$	3×10^9	7×10^{-18}	Insoluble in ammonia.
Thorium X $\downarrow$	4 days	$2\cdot00\times10^{-6}$	Soluble in ammonia.
Thorium emanation $\downarrow$	1 minute	$1\cdot15\times10^{-2}$	Chemically inert gas; condenses about $-120°$ C.
Thorium A $\downarrow$	11 hours	$1\cdot75\times10^{-5}$	Behaves as solid; insoluble in ammonia; volatilized at a white heat; soluble in strong acids; Thorium A can be separated from B by electrolysis.
Thorium B $\downarrow$	55 minutes	$2\cdot1\times10^{-4}$	
Thorium C (final product)	—	—	
ACTINIUM $\downarrow$	—	—	
Actinium X ? $\downarrow$	—	—	
Actinium emanation $\downarrow$	$3\cdot7$ seconds	$1\cdot87\times10^{-1}$	Behaves as a gas.
Actinium A $\downarrow$	41 minutes	$2\cdot80\times10^{-4}$	Behaves as solid; soluble in strong acids; A can be partially separated from B by electrolysis.
Actinium B $\downarrow$	$1\cdot5$ minutes	$7\cdot7\times10^{-3}$	
Actinium C (final product)	—	—	
RADIUM $\downarrow$	800 years	$2\cdot8\times10^{-11}$	
Radium emanation $\downarrow$	4 days	$2\cdot00\times10^{-6}$	Chemically inert gas; condenses about $-150°$ C. Definite spectrum; volume diminishes with time.
Radium A $\downarrow$	3 minutes	$3\cdot8\times10^{-3}$	Behaves as solid; soluble in strong acids; volatilized at a white heat; B is more volatile than A or C and can thus be temporarily separated from them.
Radium B $\downarrow$	21 minutes	$5\cdot38\times10^{-4}$	
Radium C $\downarrow$	28 minutes	$4\cdot13\times10^{-4}$	
Radium D $\downarrow$	About 40 years	—	Gives out only β rays. Soluble in strong acids.
Radium E $\downarrow$	About 1 year	—	Probably active constituent of radio-tellurium; soluble in strong acids; volatilized at a red heat: deposited on bismuth in solution.

The value of T may be taken as a comparative measure of the stability of the atoms of each product. The atoms of the radium emanation and thorium X have about the same stability. The apparent agreement of the rate of change in the two cases must be considered as a coincidence, and does not, in any way, indicate that the atoms of the two products are the same, for ThX and the radium emanation differ both in physical and chemical properties. If the atoms of the two products were identical, it would be expected that the subsequent changes would take place in the same way and at the same rate; but such is not the case. The stability of the atoms of the products varies over a very wide range. The stability of the atom of ThX, for example, is about 100,000 times greater than that of the actinium emanation. There is every reason to believe that the radio-elements themselves must be regarded as radioactive products of very slow rate of change. In a case like uranium, which is probably half transformed in about 1,000,000,000 years, the atoms must be considered as very stable compared with products like the emanations of thorium or radium.

27. *Rayless Changes.*—The existence of a well-marked change in radium, thorium, and actinium, which is not accompanied by the expulsion of α or β particles, is of great interest and importance.

Since the rayless changes are not accompanied by any appreciable ionization of the gas, their presence cannot be detected by direct means. The rate of change of the substance can, however, be indirectly determined, as we have seen, by determination of the variation with time of the activity of the succeeding product. The law of change has been found to be the same as for the changes which give rise to α rays. The rayless changes are thus analogous, in some respects, to the monomolecular changes observed in chemistry, with the difference that the changes are in the atoms themselves, and are not due to a molecular combination of the atoms with another substance.

It must be supposed that a rayless change is not of so violent a character as one which gives rise to the expulsion of α or β particles. The change may be accounted for either by supposing that there is a re-arrangement of the components of the atom, or that the atom breaks up without the expulsion of its parts with sufficient velocity to produce ionization by collision with the gas. The latter point of view, if correct, at once indicates the possibility that changes of a similar character may be taking place slowly in the non-radioactive elements; or, in other words, that all matter may be undergoing a slow process of change. The changes taking place in the radio-elements have been detected only in consequence of the expulsion with great velocity of the parts of the disintegrated atom. If the α particles had been expelled with a velocity less than 10^8 centims. per second, it is improbable that any ionization would have been produced, and the changes, in consequence, could not have been followed by the electric method.

28. *Radiations from the Products.*—The radiations from the successive products of

the disintegration of radium have been very closely investigated, and it has been found that, with the exception of the rayless change, all the changes are accompanied by the emission of α particles with great velocity. The β and γ rays appear only in the fifth change. In the case of thorium, it has not been found possible to completely free the product ThX from β rays, on account of the difficulty of entirely removing from it the products of the subsequent change. The proportion of β rays is, however, greatly reduced if the emanation produced by the ThX is removed by passing a rapid current of air through a solution of ThX. The emanation itself gives out only α rays, but the second product, thorium B, arising from it gives out all three types of rays. A removal of part of the emanation thus decreases the amount of β rays from the ThX. I think there is little doubt that, if the emanation could be removed from the ThX as fast as it was formed, it would be found that the ThX itself gives out only α rays, and that the β and γ rays, as in the case of radium, appear only in the fifth change.

It is remarkable that the β and γ rays of uranium, thorium, and radium appear only in the last of the rapid succession of changes occurring in those bodies. It has already been pointed out that the β and γ rays always appear together and in the same proportion. There is now little doubt that the γ rays are electromagnetic pulses, similar to X rays, generated at the moment of the sudden expulsion of the β particle from the radio-atom.

In the three radio-elements, the expulsion of the β particle results in the appearance of a product either permanently stable, or, in the case of radium, of a product far more stable than the preceding one. It would appear that the initial changes are accompanied only by the expulsion of an α particle, and that once the β particle is expelled, the components of the residual atom fall into an arrangement of fairly stable equilibrium, when the rate of disintegration is very slow. I think that it is more than a coincidence that the β and γ rays appear only in the last of the rapid changes in the three radio-elements.

It appears probable that the β particle, which is finally expelled, may be regarded as the active agent in promoting the disintegration of the radio-atom in successive stages. According to the modern point of view of regarding atomic structure, the atoms of the radio-element may be supposed to be made up of electrons (β particles) and groups of electrons (α particles) in rapid motion, and held in equilibrium by their mutual forces. If the atom is to remain permanently stable, it is necessary that there should be no loss of energy as a whole from the moving charged parts of which the atom is built up. LARMOR has shown that this condition is fulfilled if the vector sum of the accelerations of the moving particles is permanently null. If this is not the case, there must be a continuous drain of energy from the atom in the form of electromagnetic radiation. This, in the course of time, must disturb the equilibrium of the atom, and result either in a re-arrangement of its component parts or to its final disintegration. It may, perhaps, be supposed that occasionally one of the

outlying revolving electrons, comprising the radio-atom, lapses into a position which results in a slow loss of energy from the atom in the form of radiation. In consequence of this loss of energy, the atom becomes unstable, and ultimately an α particle flies off with its great orbital velocity, but the atom still retains the disturbing cause. The residue, in consequence, again becomes unstable and ejects another α particle, and the process goes on from stage to stage, until finally the β particle is violently ejected from the system.

Following the general point of view suggested by Sir OLIVER LODGE in a recent letter to 'Nature,' it may be possible that, as a result of continuous radiation, the velocity of the β particle in its orbit has steadily increased, until finally in the last stage a sudden lapse into a new state of the atom occurs, in which not only does an α particle escape, but also the β particle. When the β particle is removed from it, the residual atom adjusts itself again into a position of more permanent equilibrium.

The experimental evidence as a whole points strongly to the conclusion that the change in which the β rays appear is far more disruptive in character than any of the preceding ones; for not only is the β particle thrown off with nearly the velocity of light, but the α particle, ejected at the same time, has greater penetrating power and probably greater kinetic energy than in any of the other changes.

In addition, there is at present some evidence that this final change is of such a violent character that the atom is in some cases disrupted into several fragments, and that, in addition to the α and β particles, two or more atoms are produced, each of which has some distinctive physical and chemical properties, and also a distinctive rate of decay. If the greater proportion of the matter resulting from the disintegration is of one kind, it would be difficult to detect the presence of a small quantity of rapidly changing matter from observations of the curves of decay; but if the products have distinctive electrochemical behaviour, a partial separation, in some cases, should be effected by electrolysis. The electrolytic method is a very powerful means of separating active products which may be present in small quantity compared with the other radioactive products. It has already been mentioned (section 13) that the results of PEGRAM and VON LERCH, obtained by electrolysis of thorium solutions, may be in part explained on the supposition that thorium A and thorium B have distinctive electrochemical behaviour. PEGRAM, however, in addition, observed the presence of a product which lost half of its activity in about 6 minutes. This active product was obtained by electrolysing a solution of pure thorium salt, to which a small quantity of copper nitrate was added. The copper deposit was found to be radioactive to a slight extent, and the activity decayed to half value in about 6 minutes.

The presence of such radioactive products, which do not come under the main scheme of changes, indicates that at some stage of the disintegration more than one radioactive substance results. In the violent disintegration which occurs in radium C and thorium B, such a result is to be expected; for it is not improbable that there

are several arrangements of the constituents of the atoms to form a system of some slight stability. The two radioactive products resulting from the disintegration of a single atom would probably be present in unequal proportions. A closer investigation of the radioactive bodies will very probably lead to the separation of a number of radioactive products, present in a small proportion among the main products.

29. *Difference between Radioactive and Chemical Change.*—The successive changes occurring in the radio-elements are distinguished in certain important particulars from ordinary chemical change. We have seen that each active product, left to itself, is transformed according to a definite law and at a definite rate. The law of change is the same as for a monomolecular reaction in chemistry, and shows that only one changing system is involved. The constant of change λ is independent of the degree of concentration of the product, and of the nature and presence of the surrounding gas, and, in most cases, is not much affected by wide differences of temperature. The work of CURIE and DANNE, however, shows that the constant λ of the product radium C (see section 21) is certainly altered by temperature. After this substance has been subjected for a few minutes to a temperature of about 1100° C., its value of λ (when cooled to atmospheric temperature) *is permanently altered*. The value of λ at 1100° C. is about 1·4 times the normal value. Above 1100° C. the value of λ decreases again, and at 1300° C. it is about 1·1 times the normal. These results show that increase of temperature to a certain point increases the rate of disintegration of radium C, but that on exposure to a still higher temperature the rate of disintegration decreases again and becomes nearly equal to the normal value.

The two features which differentiate the radioactive changes from ordinary chemical change are :—

(1) The expulsion of charged particles with great velocity ;
(2) The emission of an enormous amount of energy compared with the amount of matter involved.

Except in the case of the radio-elements, no chemical change is known which is accompanied by an expulsion with great velocity of a product of the change. In each change that is accompanied by the expulsion of α rays, the amount of energy liberated, weight for weight, is over 100,000 times greater than has previously been observed in any chemical reaction. Dr. BARNES and the writer[*] showed that 75 per cent. of the heat-emission of radium was due to the emanation and its further products. The emanation from a gramme of radium gives out heat at the rate of 75 gramme-calories per hour. The total amount of heat liberated during its life is 10,000 gramme-calories approximately. Now from the work of RAMSAY and SODDY it is known that the volume of the emanation extracted from 1 gramme of radium is not greater than 1 cub. millim. The energy emitted from 1 cub. centim. of the radium emanation is

[*] ‘Phil. Mag.,’ February, 1904.

therefore equal to 10^7 gramme-calories. Now the heat emitted during the combination of 1 cub. centim. of hydrogen and oxygen to form water is 2 gramme-calories. Thus the emanation gives out during its changes 5×10^6 times as much energy as the combination of an equal volume of hydrogen and oxygen to form water. The energy emitted from a vessel containing the radium emanation is almost equally divided between the emanation and the products radium A and radium C. Each of these products gives out α rays. It is probable that the 'rayless' product radium B gives out far less heat than the other products.

There seems to be little doubt that the energy emitted from radium is about equally divided between the products which break up with the expulsion of α particles, *i.e.*, 25 per cent. of the total heat emission is supplied in each case by the breaking up of radium, the emanation, radium A and radium C. The energy radiated is, in all probability, mainly derived from the kinetic energy of the expelled α particles. Since the α particles expelled from the products of uranium, thorium, and actinium are projected with about the same velocity as from radium, it necessarily follows that each atom of the radioactive products which breaks up with the expulsion of α particle gives out about an equal quantity of energy. This amount of energy is about 6×10^{-6} erg for each atom at each stage of its disintegration.

Since there is the same number of changes in thorium as in radium, the heating effect of thorium will be proportional to its activity, *i.e.*, will be only about 5×10^{-7} of that from an equal quantity of radium.

Since the discovery of the actual production of helium from the radium emanation by RAMSAY and SODDY, there has been a tendency to assume that helium is the final transformation product of radium. There is no evidence in support of such a conclusion, for, as we have already seen, the radium atom goes on through a further series of slow changes after the first rapid changes have taken place during which the helium makes its appearance. In addition, the evidence supports the view that one α particle is expelled from each atom at each stage of its disintegration, excepting possibly the rayless change. The expulsion of four α particles, of mass about that of the helium atom, still leaves a heavy atom behind. I have previously pointed out that the α particles, in all probability, consist of helium atoms expelled at the successive stages of the disintegration. This conclusion is supported by measurements of the mass of the α particle, and by the observations of the rate of production of helium by the radium emanation made by RAMSAY and SODDY.

The similarity of the α particles from the different radio-elements indicates that they consist of expelled particles of the same kind. On this view, helium should be produced by each of the radio-elements. The presence of helium in minerals such as thorium, for example, in monazite sand, and the Ceylon mineral described by RAMSAY, suggests that helium is a product of thorium as well as of radium.

Taking the view that the α particles are projected helium atoms, we must regard the atoms of the radio-elements as compounds of some known or unknown substance

with helium. These compounds break up spontaneously and at a very slow rate even in the case of radium. The disintegration takes place in successive stages, and at most of the stages a helium atom is projected with great velocity. This disintegration is accompanied by an enormous emission of energy. The liberation of such a large amount of energy in the radioactive changes at once explains the independence of the rate of change on the physical and chemical agencies at our command. On this view, uranium, thorium and radium are in reality compounds of helium. The helium, however, is held in such strong combination that the compound cannot be broken up by chemical or physical forces and, in consequence, these bodies behave as chemical elements in the ordinary accepted chemical sense.

It appears not unlikely that many of the so-called chemical elements may prove to be compounds of helium, or, in other words, that the helium atom is probably one of the secondary units with which the heavier atoms are built up.

30. *The Charge Carried by the α Rays.*—It is of great importance to determine as directly as possible the total number of α particles expelled from a known weight of radium in order to deduce the number of atoms which break up per second. The most direct method of determining this number is to measure the positive charge carried off by the α rays. Assuming that the charge of the α particle is equal in magnitude to that carried by the ions in gases, the number of α particles expelled per second can at once be determined.

A thin film of radium was obtained on a plate by evaporation of a radium bromide solution of known strength. Some hours after evaporation, the activity of radium measured by the α rays is about 25 per cent. of its maximum value, and the β rays are almost completely absent. The arrangement of the experiment is shown in fig. 16.

The active plate A was insulated in a metal vessel, C, and was connected to one pole of the battery, the other pole being earthed. The upper plate B was insulated and connected to a Dolezalek electrometer. The outside vessel C could be connected to either A or B, or to earth. By means of a mercury pump, the vessel C was exhausted to a very low pressure. If the α rays carried a positive charge, the current between the two plates measured by the electrometer should be greater when A is charged positive than when A is negative. No appreciable difference, however, between the currents in the two directions was observed even when a very good vacuum was obtained. In addition, it was found that the current between the plates at first diminished rapidly with the pressure, but reached a limiting value which was not altered by further lowering the pressure. These results are very difficult of interpretation. There is no doubt that the α particle behaves as a positively charged body, inasmuch as it is deviated in a magnetic and electric field in the opposite direction to the β particle. The failure to detect the charge carried by the α rays is probably due in part to a strong secondary ionization set up by the α rays at the surface of the plates A and B. The current due to this effect does not diminish with

pressure below a certain limit, and does not seem to be much altered if the air is replaced by hydrogen. At the same time, taking the estimate of the number of particles from 1 gramme of radium, discussed in section 31, it was deduced that the
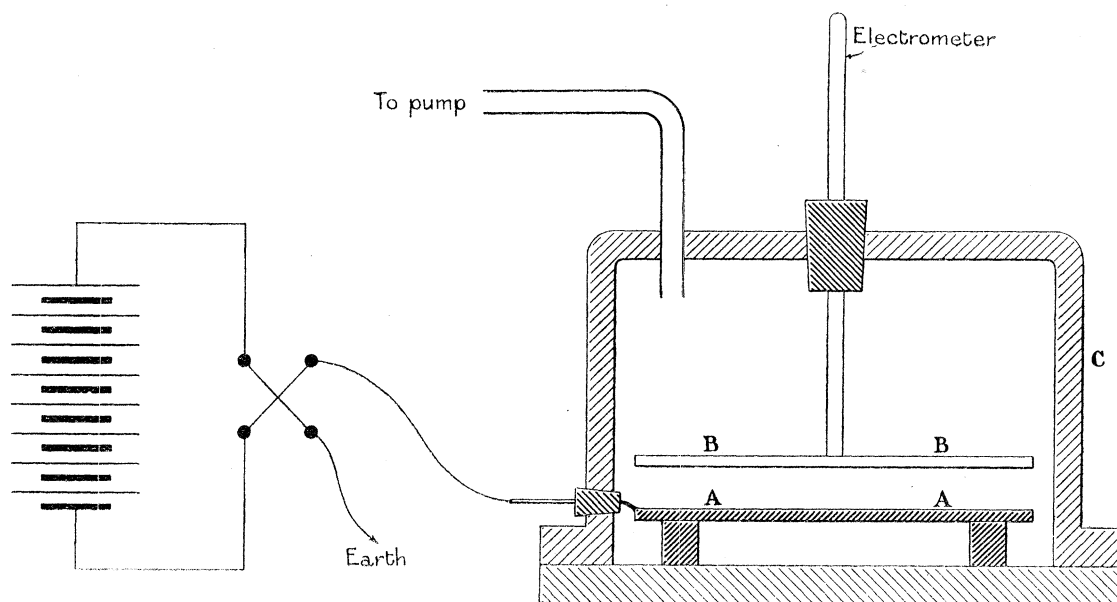

Fig. 16.

charge carried by them should certainly have been detected by reversal of the electric field, notwithstanding the presence of surface ionization.

A large number of experiments have been made under different conditions, but the results have so far all been negative. It is very difficult to avoid the conclusion that the α particles do carry with them a positive charge, but it must be supposed that the effect of this charge is in some way exactly neutralized. In this connection, it is significant that the charge carried by the 'canal rays,' which are analogous to the α rays of the radio-elements, has not so far been detected, although careful experiments upon that point have been made by WIEN. The apparent absence of charge on the α particles would be explained if an equal number of negatively charged particles, or electrons, were expelled at the same time with a slow velocity. If the electrons had about the same penetrating power as the α particles, it would be difficult to detect their presence by the electric method, as the ionization produced by the α particles would probably mask that produced by the electrons. The electron should be readily deflected in a magnetic field and experiments are, at present, in progress to examine whether the α rays show any trace of positive charge when the rays are exposed to a strong magnetic field.

31. *Magnitude of the Changes Occurring in the Radio-elements.*—I have shown ('Radioactivity,' pp. 154–158) that probably about 10^{11} of the α particles are expelled

per second from 1 gramme of radium in radioactive equilibrium. This estimate has been deduced as an average of three distinct methods of calculation based on—

(1) The charge carried off by the β rays;
(2) The energy required to produce an ion;
(3) The number of ions produced per centimetre of path by an α particle.

A check on this estimate can be made from calculations of the heating effect observed in radium. There is little doubt that the heating effect of radium is due mainly to the bombardment of the radium by the α particles expelled from its substance. Now, since $e/m = 6.3 \times 10^3$ for the α particle, and the velocity v is 2.5×10^9, the kinetic energy of the α particle is $\frac{1}{2}mv^2 = \frac{1}{2}\frac{m}{e} . v^2 . e = 6 \times 10^{-6}$ erg, if the charge $e = 3.4 \times 10^{-10}$ electrostatic unit.

The rate of heat emission from 1 gramme of radium is equal to 100 gramme-calories per hour, i.e., is mechanically equivalent to 1.2×10^6 ergs per second. If the heating effect is supposed to be due to the kinetic energy of the expelled α particles, 2×10^{11} α particles must be expelled per second to account for the heat emission. This number is in good accordance with the calculated estimate already given. Knowing the number of α particles expelled per second, the volume of the emanation stored up in 1 gramme of radium can at once be deduced. For the purpose of calculation, it is assumed that each atom in breaking up gives rise to one α particle and to one atom of the succeeding product. This is supported by the observed result, that each active product of radium supplies almost an equal proportion of the total activity measured by the α rays, i.e., each active product expels about the same number of rays. Now, α rays are expelled by the radium itself, by the emanation, and the products radium A and C. The amount of the slowly changing products radium D and E present is too small to take into account. There are thus four α particles expelled for each radium atom which breaks up. There are thus 2.5×10^{10} atoms of radium breaking up per second. In a state of radioactive equilibrium the number n of atoms of emanation present per gramme of radium is given by $n/q = 1/\lambda$, where q is the number supplied per second, or the number of radium atoms breaking up per second, λ is the radioactive constant. Since $1/\lambda = 500,000$ for the emanation, and $q = 2.5 \times 10^{10}$, we have $n = 1.25 \times 10^{16}$. TOWNSEND showed that $Ne = 1.21 \times 10^{10}$, where N is the number of molecules of hydrogen per unit volume at atmospheric pressure and temperature.

Taking J. J. THOMSON's value of e, 3.4×10^{-10} electrostatic unit, we find $N = 3.6 \times 10^{19}$. The volume of the emanation from 1 gramme of radium is n/N cub. centims., which is $\dfrac{1.25 \times 10^{16}}{3.6 \times 10^9}$, or 3.5×10^{-4} cub. centim., at standard pressure and temperature.

Now, RAMSAY and SODDY have recently isolated the emanation, and deduced that the volume from 1 gramme was equal to about 1 cub. millim. The calculated volume

is thus of the right order of magnitude. The agreement would be still closer if the number of α particles were taken as 2×10^{11}, the number deduced from the heating effect of radium, rather than 10^{11}. It is probable that the volume obtained by RAMSAY and SODDY is a maximum estimate, on account of the difficulty of removing traces of other gases.

We may thus conclude with some confidence that about 2×10^{11} α particles are expelled per second per gramme, and that the number of atoms per gramme breaking up per second is 5×10^{10}.

Since 1 cub. centim. of hydrogen contains $3 \cdot 6 \times 10^{19}$ molecules, it can readily be deduced that 1 gramme of radium contains $1 \cdot 8 \times 10^{21}$ atoms, taking the atomic weight of radium as 225.

The fraction of radium breaking up is thus $\dfrac{5 \times 10^{10}}{1 \cdot 8 \times 10^{21}}$, or $2 \cdot 8 \times 10^{-11}$ per second, that is, $8 \cdot 8 \times 10^{-4}$ per year. Thus in a gramme of radium almost one milligramme breaks up per year.

Now there is every reason to suppose that the amount of radium breaking up per second is always proportional to the amount present, as in the case of all the active products. If N_0 is the number of atoms initially present, the number N_t at any time t is given by $N_t/N_0 = e^{-\lambda t}$, where λ is equal to the fraction of the radium disintegrating per second, $i.e.$, for radium $\lambda = 2 \cdot 8 \times 10^{-11} \, (\text{sec})^{-1} = 8 \cdot 8 \times 10^{-4} \, (\text{year})^{-1}$.

The time taken for the radium to be half transformed will be about 800 years; while the $average\ life$ of the radium is λ^{-1}, or 1100 years approximately.

Now, pure radium bromide has an activity nearly 2,000,000 times that of uranium, measured by the α rays, and the activity of thorium, weight for weight, is about the same as uranium. Taking, as a first approximation, that the activity is proportional to the number of α particles expelled, it can readily be deduced that in thorium, where there are four products which expel α rays, as in the case of radium, the $average\ life$ λ^{-1} is $1100 \times 2 \times 10^6$, or 2×10^9 years.

In uranium, where there is only evidence of one change emitting α rays, the average life is only one quarter as long, $i.e.$, 5×10^8 years.

Since each radio-atom expels one α particle of atomic weight about that of hydrogen or helium, the atoms of the intermediate products will not differ much in weight from the parent atom.

The approximate weight of each product present in a gramme of radium can be readily deduced. Let N_A, N_B, N_C be the number of atoms of the products A, B, C present per gramme in radioactive equilibrium. Let λ_A, λ_B, λ_C be the corresponding constants of change. Then if q is the number of the parent atoms breaking up per second,

$$q = \lambda_A N_A = \lambda_B N_B = \lambda_C N_C.$$

Consider the case of the radium products where the value of q is 5×10^{10} per

gramme.   The value of N for each of the products is shown in the following table, along with the corresponding weights :—

Product.	Value of λ (sec)$^{-1}$.	Number of atoms present per gramme.	Weight of product in milligrammes.
Radium emanation	$2 \cdot 0 \times 10^{-6}$	$2 \cdot 5 \times 10^{16}$	$1 \cdot 4 \times 10^{-2}$
Radium A	$3 \cdot 8 \times 10^{-3}$	$1 \cdot 3 \times 10^{13}$	7×10^{-6}
Radium B	$5 \cdot 4 \times 10^{-4}$	9×10^{13}	5×10^{-5}
Radium C	$4 \cdot 1 \times 10^{-4}$	$1 \cdot 2 \times 10^{14}$	7×10^{-5}

With the small quantities of radium available, the amounts of the products radium A, B, and C are too small to weigh.   It may be possible, however, to detect their presence by means of the spectroscope.

In the case of thorium, the weight of product ThX, which is present in greatest quantity, is far too small to detect.   Since the value of λ for ThX is about the same as for the radium emanation, the maximum weight present per gramme is about $1/2 \times 10^{-6}$ of the weight of the emanation, *i.e.*, about 10^{-11} gramme.   Even from a kilogramme of thorium, the amount of ThX is too small to detect by its weight.

The evidence at present obtained points strongly to the conclusion that the expelled α particle becomes helium after its charge is neutralized.   If this is the case, the volume of helium produced from radium per year can at once be estimated. Since the emanation, radium A, and radium C, expel α particles, the volume of helium produced during the life of the emanation should be three times the initial volume of the emanation.   It is difficult to estimate experimentally the volume of helium produced, on account of its absorption by the walls of the tube, but the experiments of RAMSAY and SODDY show it is about this order of magnitude.   Since 2×10^{11} atoms of helium are expelled per second, the number expelled per year is $6 \cdot 3 \times 10^{18}$.   The volume of helium produced per gramme of radium per year is $\dfrac{6 \cdot 3 \times 10^{18}}{3 \cdot 6 \times 10^{19}}$, or $\cdot 18$ cub. centim.

32. *Origin of the Radio-elements.*—We have seen that 1/1000 of a given quantity of radium is transformed per year and half after a period of 800 years.   At the end of 8000 years only about 1/1000, and at the end of 16,000 years only $1/10^6$ of a given quantity of radium would remain unchanged.   Thus if the whole earth had been initially composed of pure radium, its activity 16,000 years later would not be greater than a good specimen of pitchblende to-day.   Since there is little doubt that the radioactive minerals are very much older than this, we are forced to the conclusion

that radium must be produced from some source, and that the present supply is maintained by the continuous production of fresh radium to balance its rate of disappearance.

The question of possible parentage has been discussed by the writer ('Radio-activity,' p. 334) and it has been shown that uranium best fulfils the conditions of being the parent of radium. In the first place, uranium has an average life 5×10^8 years, which is very long compared with the life of radium. In addition, the activity observed in pitchblende is about what would be expected if uranium were the parent of radium. If each atom of uranium in breaking up gives rise to one atom of radium, the activity of the uranium and its products (measured by the α rays) would be about six times that of the uranium itself. This follows since each atom of uranium in breaking up gives out only one α particle, while the radium arising from it would give out during its succession of changes five α particles (including the α particle from radium E).

Taking into account that actinium and thorium, as well as uranium and radium, are found in pitchblende, the observed activity of about six or seven times that of uranium is almost what is to be expected if radium is a product of uranium.

Now, from the data given in section 31, the amount of radium produced per year on the above hypothesis can readily be calculated. The fraction of uranium changing per year is about 2×10^{-9}. Assuming that the uranium passes directly through rapid stages into radium, the weight of radium produced per year, per gramme of uranium, would be nearly equal to the weight of uranium changed, i.e., 2×10^{-9} gramme. The emanation from this quantity of radium would discharge an ordinary electroscope in about 10 minutes, and thus a very small fraction of the above amount should be detectable. If a kilogramme of uranium is used instead of a gramme, the amount of radium produced per year is 2×10^{-6} gramme. The emanation from this amount would discharge an electroscope almost instantly. The amount of radium produced in a single day should be readily recognizable.

The suggestion that uranium was a possible parent of radium was given in the paper on 'Radioactive Change,' and it was arranged between Mr. SODDY and the writer that the former should try experiments to ascertain whether radium were produced from uranium. Mr. SODDY has published a preliminary account of his experiments.* He found no evidence of the production of radium from uranium and calculated that if radium were produced at all, it was certainly at less than 1/100,000 of the theoretical rate.

On my part, I have examined both thorium and actinium to find whether radium is produced from them. It was thought possible that actinium might be an intermediate product between uranium and radium. The theoretical outlook for thorium did not seem very promising, but the observation that some pure thorium

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* 'Nature,' May, 1904.

nitrate, obtained from Dr. KNÖFFLER, of Berlin, gave off a considerable quantity of radium emanation, led me to examine thorium as well as actinium.

About 500 grammes of thorium nitrate was taken and dissolved in water. A small quantity of barium nitrate was mixed with it and sufficient sulphuric acid added to precipitate the barium as sulphate. After two successive precipitations all but a small percentage of the radium was removed with the barium. The treated thorium solution was then placed in a closed glass vessel and the emanation allowed to collect in the air-space above the solution. The air was drawn off at intervals and passed into a suitable electroscope. The rate of discharge observed was proportional to the amount of emanation present and thus served as a convenient means of determining the variation from time to time of the amount of radium in the solution.

In a similar way, some of GIESEL's emanating substance was dissolved in acid and the radium removed by precipitation with barium. The solution has been set aside in a stoppered bottle and the amount of emanation present determined from time to time.

The observations on actinium have been in progress for three months and for thorium about four months. The earlier observations seemed to indicate a change of the amount of radium present in both the actinium and thorium solutions, but later observations show that if radium is produced at all, it is produced at a very small fraction of the theoretical rate. The experiments on thorium and actinium are being continued, and in the course of a few years it is hoped that a definite answer to the question will be given.

In experiments of this character certain precautions are essential in order to avoid large possible sources of error in deducing the amount of emanation present by means of the rate of discharge of an electroscope. These sources of error are especially marked in experiments with solutions of thorium or actinium. The emanations from these substances escape into the air-space above the solution. If any dust or water globules are present, excited activity is produced on them. On removal of the air these active carriers are removed with it and unless they are allowed time to settle, or removed by passage through a filter of cotton wool, they are carried into the electroscope and produce an increased rate of discharge. I have found that if the air after removal is stored over water in a gas-holder for an hour the carriers of excited activity are removed from the gas. The effect in the electroscope is then due to the emanation alone.

No definite experimental evidence is yet forthcoming that radium can be produced by uranium, thorium or actinium. It is not unlikely, however, that the negative results so far obtained may be due to the presence of one or more rayless changes between the parent substance and the radium. We have seen that such rayless changes exist in radium, thorium and actinium, and the failure to detect the production of radium would be explained if the intervening 'rayless' products were removed by the same chemical operation which freed the substance of radium.

There is one direct method of attack of the question. If uranium is the parent of radium, the amount of radium for different pitchblendes should always be proportional to the amount of uranium present.* The origin of the other radio-elements could be attacked in a similar way.

The whole subject of the relative connection and origin of the radio-elements is of the greatest interest and importance. The close similarity of the changes in radium, thorium and actinium is very remarkable and indicates some peculiarity of atomic constitution which still remains to be elucidated.

* BOLTWOOD has recently published some numbers ('Nature,' May 25, 1904, p. 80) which seem to show that in the pitchblendes examined the amount of radium is strictly proportional to the amount of uranium in the mineral. Further results of this character are very much required.