

be a mere point; the region of misfit (to borrow an expressive term from Prof. Osborne Reynolds) might, if necessary, have definite extension and structure. Hypotheses of this type are most naturally (indeed, as it seems to me, unavoidably) expressed in terms of an æther which is only locally disturbed by each moving ion; so that a congeries of connected atoms like the Earth does not push it along bodily and establish any finite flow. But there may be philosophers who prefer not to employ the term æther at all, who are satisfied with a colourless phenomenology, and who manage to escape the consideration of the possibility of an æther whose parts maintain their positions notwithstanding the motion of matter through it, by saying merely that if a certain scheme of formal relations between variables which are symbols of things unknown is altered in a certain formal way, probably originally suggested by the use of dynamical analogies such as have been referred to, the scheme will continue to group the facts under the wider conditions, and they would thus feel freed from any necessity of considering images or models, probably imperfect, of things which being outside ourselves we cannot intrinsically know.

Cambridge, August 7, 1902.

XLI. *The Cause and Nature of Radioactivity.*—Part I. By E. RUTHERFORD, M.A., D.Sc., Macdonald Professor of Physics, and F. SODDY, B.A. (Oxon.), Demonstrator in Chemistry, McGill University, Montreal*.

CONTENTS.

- I. Introduction.
- II. Experimental Methods of investigating Radioactivity.
- III. Separation of a Radioactive Constituent (ThX) from Thorium Compounds.
- IV. The Rates of Recovery and Decay of Thorium Radioactivity.
- V. The Chemical Properties of ThX.
- VI. The Continuous Production of ThX.
- VII. The Influence of Conditions on the Changes occurring in Thorium.
- VIII. The Cause and Nature of Radioactivity.
- IX. The Initial Portions of the Curves of Decay and Recovery.
- X. The Non-separable Radioactivity of Thorium.
- XI. The Nature of the Radiations from Thorium and ThX.
- XII. Summary of Results.
- XIII. General Theoretical Considerations.

I. *Introduction.*

THE following papers give the results of a detailed investigation of the radioactivity of thorium compounds which has thrown light on the questions connected

* Communicated by the Authors. Accounts of these researches, during the progress of the investigation, have already been given to the London Chemical Society.

with the source and maintenance of the energy dissipated by radioactive substances. Radioactivity is shown to be accompanied by chemical changes in which new types of matter are being continuously produced. These reaction products are at first radioactive, the activity diminishing regularly from the moment of formation. Their continuous production maintains the radioactivity of the matter producing them at a definite equilibrium-value. The conclusion is drawn that these chemical changes must be sub-atomic in character.

The present researches had as their starting-point the facts that had come to light with regard to thorium radioactivity (Rutherford, *Phil. Mag.* 1900, vol. xlix. pp. 1 & 161). Besides being radioactive in the same sense as the uranium compounds, the compounds of thorium continuously emit into the surrounding atmosphere a gas which possesses the property of temporary radioactivity. This "emanation," as it has been named, is the source of rays, which ionize gases and darken the photographic film*.

The most striking property of the thorium emanation is its power of exciting radioactivity on all surfaces with which it comes into contact. A substance after being exposed for some time in the presence of the emanation behaves as if it were covered with an invisible layer of an intensely active material. If the thoria is exposed in a strong electric field, the excited radioactivity is entirely confined to the negatively charged surface. In this way it is possible to concentrate the excited radioactivity on a very small area. The excited radioactivity can be removed by rubbing or by the action of acids, as, for example, sulphuric, hydrochloric, and hydrofluoric acids. If the acids be then evaporated, the radioactivity remains on the dish.

The emanating power of thorium compounds is independent of the surrounding atmosphere, and the excited activity it produces is independent of the nature of the substance on which it is manifested. These properties made it appear that both phenomena were caused by minute quantities of special kinds of matter in the radioactive state, produced by the thorium compound.

The next consideration in regard to these examples of radioactivity, is that the activity in each case diminishes regularly with the lapse of time, the intensity of radiation at each instant being proportional to the amount of energy remaining to be radiated. For the emanation a period of

* If thorium oxide be exposed to a white heat its power of giving an emanation is to a large extent destroyed. Thoria that has been so treated is referred to throughout as "de-emanated."

one minute, and for the excited activity a period of eleven hours, causes the activity to fall to half its value.

These actions—(1) the production of radioactive material, and (2) the dissipation of its available energy by radiation—which are exhibited by thorium compounds in the secondary effects of emanating power and excited radioactivity, are in reality taking place in all manifestations of radioactivity. The constant radioactivity of the radioactive elements is the result of an equilibrium between these two opposing processes.

II. *The Experimental Methods of investigating Radioactivity.*

Two methods are used for the measurement of radioactivity, the electrical and the photographic. The photographic method is of a qualitative rather than a quantitative character; its effects are cumulative with time, and as a rule long exposures are necessary when the radioactivity of a feeble agent like thoria is to be demonstrated. In addition, Russell has shown that the darkening of a photographic plate is brought about also by agents of a totally different character from those under consideration, and, moreover, under very general conditions. Sir William Crookes (Proc. Roy. Soc. (1900) lxvi. p. 409) has sounded a timely note of warning against putting too much confidence in the indications of the photographic method of measuring radioactivity. The uncertainty of an effect produced by cumulative action over long periods of time quite precludes its use for work of anything but a qualitative character.

But the most important objection to the photographic method is that certain types of rays from radioactive substances, which ionize gases strongly, produce little if any effect on the sensitive film. In the case of uranium, these protographically inactive rays form by far the greatest part of the total radiation, and much of the previous work on uranium by the photographic method must be interpreted differently (Soddy, Proc. Chem. Soc. 1902, p. 121).

On the other hand, it is possible to compare intensities of radiation by the electrical method with greater rapidity and with an error not exceeding 1 or 2 per cent. These methods are based on the property generally possessed by all radiations of the kind in question, of rendering a gas capable of discharging both positive and negative electricity. These, as will be shown, are capable of great refinement and certainty. An ordinary quadrant electrometer is capable of detecting and measuring a difference of potential of at least 10^{-2} volts. With special instruments, this sensitiveness may be increased

a hundredfold. An average value for the capacity of the electrometer and connexions is 3×10^{-5} microfarads; and when this is charged up to 10^{-2} volts, a quantity of electricity corresponding to 3×10^{-13} coulombs is stored up. Now in the electrolysis of water one gram of hydrogen carries a charge of 10^5 coulombs. Assuming, for the sake of example, that the conduction of electricity in gases is analogous to that in liquids, this amount of electricity corresponds to the transport of a mass of 3×10^{-18} grams of hydrogen; that is, a quantity of the order of 10^{-12} times that detected by the balance. For a more delicate instrument, this amount would produce a large effect.

The examples of radium in pitchblende and of the thorium-excited radioactivity make it certain that comparatively large ionization effects are produced by quantities of matter beyond the range of the balance or spectroscope.

The electrometer also affords the means of recognizing and differentiating between the emanations and radiations of different chemical substances. By the rate of decay the emanation from thorium, for example, can be instantly distinguished from that produced by radium; and although a difference in the rate of decay does not of itself argue a fundamental difference of nature, the identity of the rate of decay furnishes at least strong presumption of identity of nature.

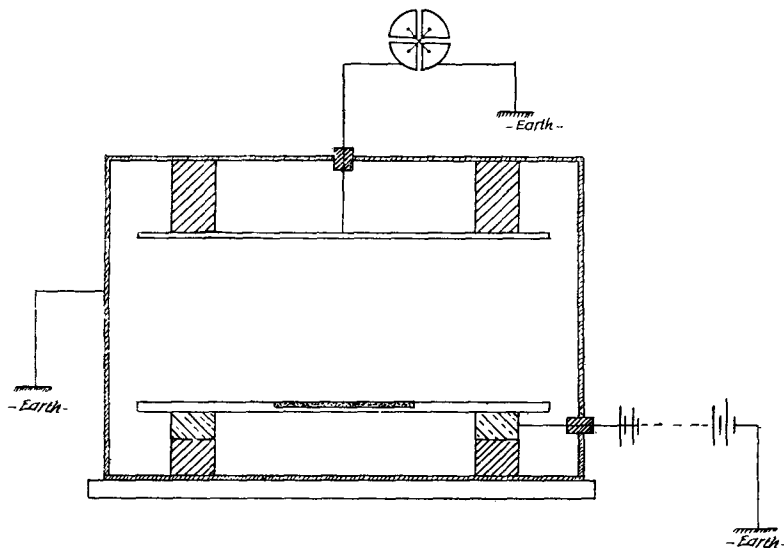
Radiations, on the other hand, can be compared by means of their penetration powers (Rutherford, *Phil. Mag.* 1899, vol. xlvii. p. 122). If the rays from various radioactive substances are made to pass through successive layers of aluminium-foil, each additional layer of foil cuts down the radiation to a fraction of its former value, and a curve can be plotted with the thickness of metal penetrated as abscissæ, and the intensity of the rays after penetration as ordinates, expressing at a glance the penetration power of the rays under examination. The curves so obtained are quite different for different radioactive substances. The radiations from uranium, radium, thorium, each give distinct and characteristic curves, whilst that of the last-named again is quite different from that given by the excited radioactivity produced by the thorium emanation. It has been recently found (Rutherford and Grier, *Phys. Zeit.* 1902, p. 385) that thorium compounds, in addition to a type of easily absorbed Röntgen-rays, non-deviable in the magnetic field, emit also rays of a very penetrating character deviable in the magnetic field. The latter are therefore similar to cathode-rays, which are known to consist of material particles travelling with a

velocity approaching that of light. But thorium, in comparison with uranium and radium, emits a much smaller proportion of deviable radiation. The determination of the proportion between the deviable and non-deviable rays affords a new means of investigating thorium radioactivity.

The electrometer thus supplies the study of radioactivity with methods of quantitative and qualitative investigation, and there is therefore no reason why the cause and nature of the phenomenon should not be the subject of chemical investigation.

Fig. 1 shows the general arrangement. From 0.5 to 0.1 gram of the compound to be tested, reduced to fine powder, is uniformly sifted over a platinum plate 36 sq. cms. in area.

Fig. 1.



This plate was placed on a large metal plate connected to one pole of a battery of 300 volts, the other pole of which was earthed. An insulated parallel plate was placed about 6 cm. above it, and the whole apparatus inclosed in a metal box connected to earth, to prevent electrostatic disturbance. The shaded portions in the figure represented insulators. A door was made in the apparatus so that the plate could be rapidly placed in position or removed. Both pairs of quadrants are first connected to earth. On connecting the one pair with the apparatus, the deflexion of the needle from zero.

increases uniformly with time, and the time taken to pass over 100 divisions of the scale is taken by a stop-watch. The *rate* of movement is a measure of the ionization-current between the plates. The ratio of the currents for different substances is a comparative measure of their radioactivity.

With this apparatus .5 gr. of thorium oxide produces a current of 1.1×10^{-11} amperes, which, with the electrometer used, working at average sensitiveness, corresponds to 100 divisions of the scale in 36 seconds. In certain cases a special modification of the Dolezalek electrometer was employed which is 100 times more sensitive. With this instrument the radioactivity of 1 milligram of thoria produces a measurable effect. If the substance gives off an emanation, the current between the plates increases with time. Under these conditions, when the thorium compound is exposed in thin layers with a maximum of radiating surface, all but one or two per cent. of the total effect is due to the straight-line radiation. Even when the effect due to the emanation has attained a maximum, this constitutes a very small fraction of the whole. This effect, however, may to a large extent be eliminated by taking the current between the electrodes immediately after the material is placed in the testing-apparatus. It may be completely eliminated by passing a current of air between the electrodes to remove the emanation as fast as it is formed.

The current between the plates observed with the electrometer at first increases with the voltage, but a stage is very soon reached when there is a very small increase for a large additional voltage. A P.D. of 300 volts was sufficient to obtain the maximum current, so that all the ions reached the electrodes before any appreciable recombination occurred.

It must, however, at once be pointed out that it is difficult to make any absolute measure of radioactivity. The radiation from thorium is half absorbed by a thickness of aluminium of .0004 cm.; and since thorium oxide is far denser than aluminium, it is probable that the radiation in this case is confined to a surface-layer only .0001 cm. deep. It is obvious that different preparations, each containing the same percentage of thorium but with different densities and different states of division, will not give the same intensity of radiation. In comparing two different specimens of the same compound, it is important that the final steps in their preparation should be the same in each case. As a rule absolute measurements of this kind have been avoided. It is possible, however, to trace with great accuracy the *change* of radioactivity of any preparation with time by leaving it undisturbed on its

original plate, and comparing it with a similarly undisturbed constant comparison sample. Most of the investigations have been carried out by this method.

III. *The Separation of a Radioactive Constituent from Thorium Compounds.*

During an investigation of the emanating power of thorium compounds, to be described later, evidence was obtained of the separation of an intensely radioactive constituent by chemical methods. It had been noticed that in certain cases thorium hydroxide, precipitated from dilute solutions of thorium nitrate by ammonia, possessed an abnormally low emanating power. This led naturally to an examination being made of the filtrates and washings obtained during the process. It was found that the filtrates invariably possessed emanating power, although from the nature of their production they are chemically free from thorium. If the filtrate is evaporated to dryness, and the ammonium salts removed by ignition, the small residues obtained exhibit radioactivity also, to an extent very much greater than that possessed by the same weight of thorium. As a rule these residues were of the order of one-thousandth part by weight of the thorium salt originally taken, and were many hundred, in some cases over a thousand, times more active than an equal weight of thorium. The separation of an active constituent from thorium by this method is not all dependent on the purity of the salt used. By the kindness of Dr. Knöfler, of Berlin, who, in the friendliest manner, presented us with a large specimen of his purest thorium nitrate, we were enabled to test this point. This specimen, which had been purified by a great many processes, did not contain any of the impurities found in the commercial salt before used. But its radioactivity and emanating power were at least as great, and the residues from the filtrates after precipitation by ammonia were no less active than those before obtained. These residues are free from thorium, or at most contain only the merest traces, and when redissolved in nitric acid do not appear to give any characteristic reaction.

An examination of the penetrating power of the rays from the radioactive residue, showed that the radiations emitted were in every respect identical with the ordinary thorium radiation. In another experiment the nature of the emanation from a similar intensely active thorium-free residue was submitted to examination. The rate of decay was quite indistinguishable from that of the ordinary thorium emanation; that is, substances chemically free from thorium have been

prepared possessing thorium radioactivity in an intense degree.

The thorium hydroxide which had been submitted to the above process was found to be less than half as radioactive as the same weight of thorium oxide. It thus appeared that a constituent responsible for the radioactivity of thorium had been obtained, which possessed distinct chemical properties and an activity of the order of at least a thousand times as great as the material from which it had been separated.

Sir William Crookes (Proc. Roy. Soc. 1900, lxvi. p. 409) succeeded in separating a radioactive constituent of great activity and distinct chemical nature from uranium, and gave the name UrX to this substance. For the present, until more is known of its real nature, it will be convenient to name the active constituent of thorium ThX, similarly. Like UrX, however, ThX does not answer to any definite analytical reactions, but makes its appearance with precipitates formed in its solution even when no question of insolubility is involved. This accords with the view that it is present in infinitesimal quantity, and possesses correspondingly great activity. Even in the case of the most active preparations, these probably are composed of some ThX associated with accidental admixtures large in proportion.

These results receive confirmation from observations made on a different method of separating ThX. The experiment was tried of washing thoria with water repeatedly, and seeing if the radioactivity was thereby affected. In this way it was found that the filtered washings, on concentration, deposited small amounts of material with an activity often of the order of a thousand times greater than that of the original sample. In one experiment, 290 grams of thoria were shaken for a long time with nine quantities, each of 2 litres of distilled water. The first washing, containing thorium sulphate present as an impurity, was rejected, the rest concentrated to different stages and filtered at each stage. One of the residues so obtained weighed 6.4 mg., and was equivalent in radioactivity to 11.3 grams of the original thoria, and was therefore no less than 1800 times more radioactive. It was examined chemically, and gave, after conversion into sulphate, the characteristic reaction of thorium sulphate, being precipitated from its solution in cold water by warming. *No other substance than thorium could be detected by chemical analysis*, although of course the quantity was too small for a minute examination. The penetrating power of the radiation from this substance again established its identity with the ordinary thorium radiation.

In another experiment, a small quantity of thoria was shaken many times with large quantities of water. In this case, the radioactivity of the residue was examined and found to be about 20 per cent. less radioactive than the original sample.

The influence of Time on the activity of Thorium and ThX.—The preparations employed in our previous experiments were allowed to stand over during the Christmas vacation. On examining them about three weeks later it was found that the thorium hydroxide, which had originally possessed only about 36 per cent. of its normal activity, had almost completely recovered the usual value. The active residues, on the other hand, prepared by both methods, had almost completely lost their original activity. The chemical separation effected was thus not permanent in character. At this time M. Becquerel's paper (*Comptes Rendus*, cxxxiii. p. 977, Dec. 9th, 1901) came to hand, in which he shows that the same phenomena of recovery and decay are presented by uranium after it has been partially separated from its active constituent by chemical treatment.

A long series of observations was at once started to determine—

- (1) The rate of recovery of the activity of thorium rendered less active by removal of ThX ;
- (2) The rate of decay of the activity of the separated ThX ;

in order to see how the two processes were connected. The results led to the view that may at once be stated. The radioactivity of thorium at any time is the resultant of two opposing processes—

- (1) The production of fresh radioactive material at a constant rate by the thorium compound ;
- (2) The decay of the radiating power of the active material with time.

The normal or constant radioactivity possessed by thorium is an equilibrium value, where the rate of increase of radioactivity due to the production of fresh active material is balanced by the rate of decay of radioactivity of that already formed. It is the purpose of the present paper to substantiate and develop this hypothesis.

IV. *The Rates of Recovery and Decay of Thorium Radioactivity.*

A quantity of the pure thorium nitrate was separated from ThX in the manner described by several precipitations with ammonia. The radioactivity of the hydroxide so obtained

was tested at regular intervals to determine the rate of recovery of its activity. For this purpose the original specimen of .5 gram was left undisturbed throughout the whole series of measurements on the plate over which it had been sifted, and was compared always with .5 gram of ordinary de-emanated thorium oxide spread similarly on a second plate and also left undisturbed. The emanation from the hydroxide was prevented from interfering with the results by a special arrangement for drawing a current of air over it during the measurements.

The active filtrate from the preparation was concentrated and made up to 100 c.c. volume. One quarter was evaporated to dryness and the ammonium nitrate expelled by ignition in a platinum dish, and the radioactivity of the residue tested at the same intervals as the hydroxide to determine the rate of decay of its activity. The comparison in this case was a standard sample of uranium oxide kept undisturbed on a metal plate, which repeated work has shown to be a perfectly constant source of radiation. The remainder of the filtrate was used for other experiments.

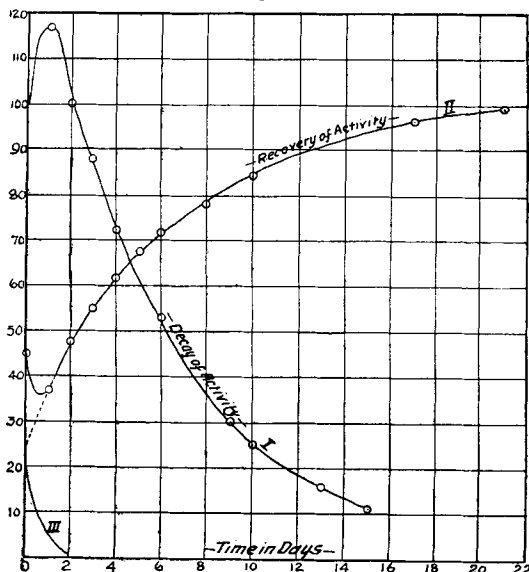
The following table gives an example of one of a numerous series of observations made with different preparations at different times. The maximum value obtained by the hydroxide and the original value of the ThX are taken as 100 :—

Time in days.	Activity of Hydroxide.	Activity of ThX.
0	44	100
1	37	117
2	48	100
3	54	88
4	62	72
5	68	
6	71	53
8	78	
9	...	29.5
10	83	25.2
13	...	15.2
15	...	11.1
17	96.5	
21	99	
28	100	

Fig. 2 shows the curves obtained by plotting the radioactivities as ordinates, and the time in days as abscissæ. Curve II. illustrates the rate of recovery of the activity of thorium, curve I. the rate of decay of activity of ThX. It

will be seen that neither of the curves is regular for the first two days. The activity of the hydroxide at first actually

Fig. 2.



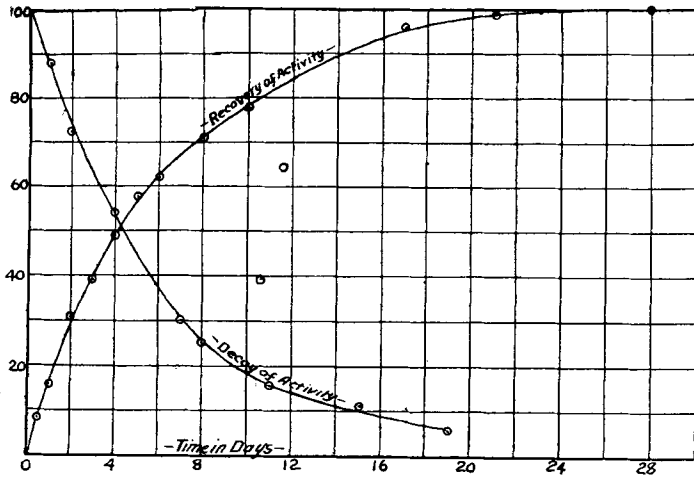
diminished and was at the same value after two days as when first prepared. The activity of the ThX, on the other hand, at first increases and does not begin to fall below the original value till after the lapse of two days (compare section IX.). These results cannot be ascribed to errors of measurement, for they have been regularly observed whenever similar preparations have been tested. The activity of the residue obtained from thorium oxide by the second method of washing decayed very similarly to that of ThX, as shown by the above curve.

If for present purposes the initial periods of the curve are disregarded and the later portions only considered, it will be seen at once that the time taken for the hydroxide to recover one half of its lost activity is about equal to the time taken by the ThX to lose half its activity, viz., in each case about 4 days, and speaking generally the percentage proportion of the lost activity regained by the hydroxide over any given interval is approximately equal to the percentage proportion of the activity lost by the ThX during the same interval. If the recovery curve is produced backwards in the normal direction to cut the vertical axis, it will be seen to do so at a

minimum of about 25 per cent., and the above result holds even more accurately if the recovery is assumed to start from this constant minimum, as, indeed, it has been shown to do under suitable conditions (section IX., fig. 4).

This is brought out by fig. 3, which represents the recovery

Fig. 3.



curve of thorium in which the percentage amounts of activity recovered, reckoned from this 25 per cent. minimum, are plotted as ordinates. In the same figure the decay curve after the second day is shown on the same scale.

The activity of ThX decreases very approximately in a geometrical progression with the time, *i. e.* if I_0 represent the initial activity and I_t the activity after time t ,

$$\frac{I_t}{I_0} = e^{-\lambda t}, \dots \dots \dots (1)$$

where λ is a constant and e the base of natural logarithms.

The experimental curve obtained with the hydroxide for the rate of rise of its activity from a minimum to a maximum value will therefore be approximately expressed by the equation

$$\frac{I_t}{I_0} = 1 - e^{-\lambda t}, \dots \dots \dots (2)$$

where I_0 represents the amount of activity recovered when the maximum is reached, and I_t the activity recovered after time t , λ being the same constant as before.

Now this last equation has been theoretically developed in other places (compare Rutherford, Phil. Mag. 1900, pp. 10 and 181) to express the rise of activity to a constant maximum of a system consisting of radiating particles in which

- (1) The rate of supply of fresh radiating particles is constant.
- (2) The activity of each particle dies down geometrically with the time according to equation (1).

It therefore follows that if the initial irregularities of the curves are disregarded and the residual activity of thorium is assumed to possess a *constant* value, the experimental curve obtained for the recovery of activity will be explained if two processes are supposed to be taking place :

- (1) That the active constituent ThX is being produced at a constant rate;
- (2) That the activity of the ThX decays geometrically with time.

Without at first going into the difficult questions connected with the initial irregularities and the residual activity, the main result that follows from the curves given can be put to experimental test very simply. The primary conception is that the major part of the radioactivity of thorium is not due to the thorium at all, but to the presence of a non-thorium substance in minute amount which is being continuously produced.

V. *Chemical Properties of ThX.*

The fact that thorium on precipitation from its solutions by ammonia leaves the major part of its activity in the filtrate does not of itself prove that a material *constituent* responsible for this activity has been chemically separated. It is possible that the matter constituting the non-thorium part of the solution is rendered temporarily radioactive by its association with thorium, and this property is retained through the processes of precipitation, evaporation, and ignition, and manifests itself finally on the residue remaining.

This view, however, can be shown to be quite untenable, for upon it any precipitate capable of removing thorium completely from its solution should yield active residues similar to those obtained from ammonia. Quite the reverse, however, holds.

When thorium nitrate is precipitated by sodium or ammonium carbonate, the residue from the filtrate by evaporation and ignition is free from activity, and the thorium carbonate possesses the normal value for its activity.

The same holds true when oxalic acid is used as the

precipitant. This reagent even in strongly acid solution precipitates almost all of the thorium. When the filtrate is rendered alkaline by ammonia, filtered, evaporated, and ignited, the residue obtained is inactive.

In the case where sodium phosphate is used as the precipitant in ordinary acid solution, the part that comes down is more or less free from ThX. On making the solution alkaline with ammonia, the remainder of the thorium is precipitated as phosphate, and carries with it the whole of the active constituent, so that the residue from the filtrate is again inactive.

In fact ammonia is the only reagent of those tried capable of separating ThX from thorium.

The result of Sir William Crookes with uranium, which we have confirmed working with the electrical method, may be here mentioned. UrX is completely precipitated by ammonia together with uranium, and the residue obtained by the evaporation of the filtrate is quite inactive.

There can thus be no question that both ThX and UrX are distinct types of matter with definite chemical properties. Any hypothesis that attempts to account for the recovery of activity of thorium and uranium with time must of necessity start from this primary conception.

VI. *The Continuous Production of ThX.*

If the recovery of the activity of thorium with time is due to the production of ThX, it should be possible to obtain experimental evidence of the process. The first point to be ascertained is how far the removal of ThX by the method given reduces the total radioactivity of thorium. A preliminary trial showed that the most favourable conditions for the separation are by precipitating in hot dilute solutions by dilute ammonia. A quantity of 5 grams of thorium nitrate, as obtained from the maker, was so precipitated by ammonia, the precipitate being redissolved in nitric acid and reprecipitated under the same conditions successively *without lapse of time*.

The removal of ThX was followed by measuring the activity of the residues obtained from the successive filtrates. The activity of the ThX from the first filtrate was equivalent to 4.25 grams of thoria, from the second to 0.33 gram, and from the third to 0.07 gram. It will be seen that by two precipitations practically the whole of the ThX is removed. The radioactivity of the separated hydroxide was 48 per cent. of that of the standard de-emanated sample of thoria.

Rate of production of ThX.—A quantity of thorium nitrate solution that had been freed from ThX about a month before, was again subjected to the same process. The activity of the residue from the filtrate in an experiment in which 10 grams of this nitrate had been employed was equivalent to 8·3 grams of thorium oxide. This experiment was performed on the same day as the one recorded above, in which 5 grams of new nitrate had been employed, and it will be seen that there is no difference in the activity of the filtrate in the two cases. In one month the activity of the ThX in a thorium compound again possesses its maximum value.

If a period of 24 hours is allowed to elapse between the successive precipitations, the activity of the ThX formed during that time corresponds to about one-sixth of the maximum activity of the total thorium employed. In three hours the activity of the amount produced is about one-thirtieth. The rate of production of ThX worked out from those figures well agrees with the form of the curve obtained for the recovery of activity of thorium, if the latter is taken to express the continuous production of ThX at a constant rate and the diminution of the activity of the product in geometrical progression with the time.

By using the sensitive electrometer, the course of production of ThX can be followed after extremely short intervals. Working with 10 grams of thorium nitrate, the amount produced in the minimum time taken to carry out the successive precipitations is as much as can be conveniently measured. If any interval is allowed to lapse the effect is beyond the range of the instrument, unless the sensitiveness is reduced to a fraction of its ordinary value by the introduction of capacities into the system. Capacities of ·01 and ·02 microfarad, which reduce the sensitiveness to less than one two-hundredth of the normal, were frequently employed in dealing with these active residues.

The process of the production of ThX is continuous, and no alteration was observed in the amount produced in a given time after repeated separations. In an experiment carried out for another purpose (section IX.) after 23 successive precipitations extending over 9 days, the amount formed during the last interval was as far as could be judged no less than what occurred at the beginning of the process.

The phenomenon of radioactivity, by means of the electrometer as its measuring instrument, thus enables us to detect and measure changes occurring in matter after a few minutes interval, which have never yet been detected by the balance or suspected of taking place.

VII. *Influence of Conditions on the Changes occurring in Thorium.*

It has been shown that in thorium compounds the decay of radioactivity with time is balanced by a continuous production of fresh active material. The change which produces this material must be chemical in nature, for the products of the action are different in chemical properties from the thorium from which they are produced. The first step in the study of the nature of this change is to examine the effects of conditions upon its rate.

Effect of conditions on the rate of decay.—Since the activity of the products affords the means of measuring the amount of change, the influence of conditions on the rate of decay must be first found. It was observed that, like all other types of temporary radioactivity, the rate of decay is unaltered by any known agency. It is unaffected by ignition and chemical treatment, and the material responsible for it can be dissolved in acids and re-obtained by the evaporation of the solution, without affecting the activity. The following experiment shows that the activity decays at the same rate in solutions as in the solid state. The remainder of the solution that had been used to determine the decay curve of ThX (fig. 2) was allowed to stand, and at the end of 12 days a second quarter was evaporated to dryness and ignited, and its activity compared with that of the first which had been left since evaporation upon its original platinum dish. The activities of the two specimens so compared with each other were the same, showing that in spite of the very different conditions the two fractions had decayed at equal rates. After 19 days a third quarter was evaporated, and the activity, now very small, was indistinguishable from that of the fraction first evaporated. Re-solution of the residues after the activity had decayed does not at all regenerate it. The activity of ThX thus decays at a rate independent of the chemical and physical condition of the molecule.

Thus the rate of recovery of activity under different conditions in thorium compounds affords a direct measure of the rate of production of ThX under these conditions. The following experiments were performed :—

One part of thorium hydroxide newly separated from ThX was sealed up in a vacuum obtained by a good Töpler pump, and the other part exposed to air. On comparing the samples 12 days later no difference could be detected between them either in their radioactivity or emanating power.

In the next experiment a quantity of hydroxide freed from

ThX was divided into two equal parts; one was exposed for 20 hours to the heat of a Bunsen burner in a platinum crucible, and then compared with the other. No difference in the activities was observed. In a second experiment, one half was ignited for 20 minutes on the blast, and then compared with the other with the same result. The difference of temperature and the conversion of thorium hydroxide into oxide thus exercised no influence on the activity.

Some experiments that were designed to test in as drastic a manner as possible the effect of the chemical condition of the molecule on the rate of production of ThX brought to light small differences, but these are almost certainly to be accounted for in another way. It will be shown later (section IX.) that about 21 per cent. of the normal radioactivity of thorium oxide under ordinary conditions consists of a secondary activity excited on the mass of the material. This portion is of course a variable, and since it is divided among the total amount of matter present, the conditions of aggregation, &c., will affect the value of this part. This effect of excited radioactivity in thorium makes a certain answer to the question difficult, and on this account the conclusion that the rate of production of ThX is independent of the molecular conditions is not final. The following experiment, however, makes it extremely probable.

A quantity of thorium nitrate as obtained from the maker was converted into oxide in a platinum crucible by treatment with sulphuric acid and ignition to a white heat. The de-emanated oxide so obtained was spread on a plate, and any change in radioactivity with time, which under these circumstances could certainly be detected, was looked for during the first week from preparation. None whatever was observed, whereas if the rate of production of ThX in thorium nitrate is different from that in the oxide, the equilibrium point, at which the decay and increase of activity balance each other, will be altered in consequence. There should have therefore occurred a logarithmic rise or fall from the old to the new value. As, however, the radioactivity remained constant, it appears very probable that the changes involved are independent of the molecular condition.

It will be seen that the assumption is here made that the proportion of excited radioactivity in the two compounds is the same, and for this reason compounds were chosen which possess but low emanating power. (Compare section IX. last paragraph.)

Uranium is a far simpler example of a radioactive element than thorium, as the phenomena of excited radioactivity and

emanating power are here absent. The separation of UrX and the recovery of the activity of the uranium with time appear, however, analogous to these processes in thorium, and the rate of recovery and decay of uranium activity are at present under investigation. It is proposed to test the influence of conditions on the rate of change more thoroughly in the case of uranium, as here secondary changes do not interfere.

VIII. *The Cause and Nature of Radioactivity.*

The foregoing conclusions enable a great generalization to be made in the subject of radioactivity. Energy considerations require that the intensity of radiation from any source should die down with time unless there is a constant supply of energy to replace that dissipated. This has been found to hold true in the case of all known types of radioactivity with the exception of the "naturally" radioactive elements—to take the best established cases, thorium, uranium, and radium. It will be shown later that the radioactivity of the emanation produced by thorium compounds decays geometrically with the time under all conditions, and is not affected by the most drastic chemical and physical treatment. The same has been shown by one of us (*Phil. Mag.* 1900, p. 161) to hold for the excited radioactivity produced by the thorium emanation. This decays at the same rate whether on the wire on which it is originally deposited, or in solution of hydrochloric or nitric acid. The excited radioactivity produced by the radium emanation appears analogous. All these examples satisfy energy considerations. In the case of the three naturally occurring radioactive elements, however, it is obvious that there must be a continuous replacement of the dissipated energy, and no satisfactory explanation has yet been put forward.

The nature of the process becomes clear in the light of the foregoing results. The material constituent responsible for the radioactivity, when it is separated from the thorium which produces it, then behaves in the same way as the other types of radioactivity cited. Its activity decays geometrically with the time, and the rate of decay is independent of the molecular conditions. The normal radioactivity is, however, maintained at a constant value by a chemical change which produces fresh radioactive material at a rate also independent of the conditions. The energy required to maintain the radiations will be accounted for if we suppose that the energy of the system after the change has occurred is less than it was before.

The work of Crookes and Becquerel on the separation of UrX and the recovery of the activity of the uranium with time, makes it appear extremely probable that the same explanation holds true for this element. The work of M. and Mme. Curie, the discoverers of radium, goes to show that this body easily suffers a temporary decrease of its activity by chemical treatment, the normal value being regained after the lapse of time, and this can be well interpreted on the new view. All known types of radioactivity can thus be brought under the same category.

IX. *The Initial Portions of the Curves of Decay and Recovery.*

The curves of the recovery and decay of the activities of thorium and ThX with time suggested the explanation that the radioactivity of thorium was being maintained by the production of ThX at a constant rate. Before this can be considered rigidly established, two outstanding points remain to be cleared up. 1. What is the meaning of the early portion of the curves? The recovery curve drops before it rises, and the decay curve rises before it drops. 2. Why does not the removal of ThX render thorium completely inactive? A large proportion of the original radioactivity is not affected by the removal of ThX.

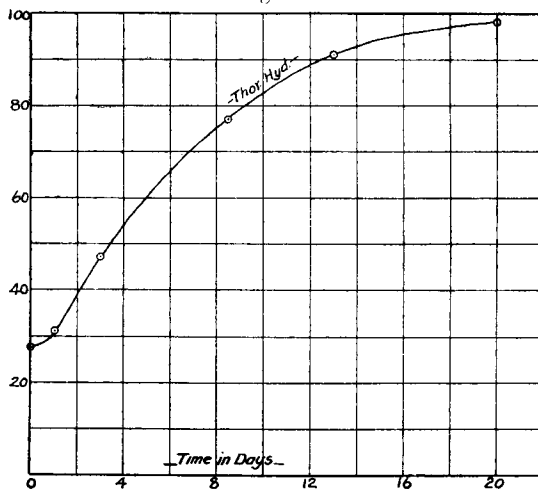
A study of the curves (fig. 2) shows that in each case a double action is probably at work. It may be supposed that the normal decay and recovery are taking place, but are being masked by a simultaneous rise and decay from other causes. From what is known of thorium radioactivity, it was surmised that an action might be taking place similar to that effected by the emanation of exciting radioactivity on surrounding inactive matter. It will be shown later that the ThX, and not thorium, is the cause of the emanating power of thorium compounds. On this view, the residual activity of thorium might consist in whole or in part of a secondary or excited radioactivity produced on the whole mass of the thorium compound by its association with the ThX. The drop in the recovery-curve on this view would be due to the decay of this excited radioactivity proceeding simultaneously with, and at first reversing the effect of the regeneration of ThX. The rise of the decay-curve would be the increase due to the ThX exciting activity on the matter with which it is associated, the increase from this cause being greater than the decrease due to the decay of the activity of the ThX. It is easy to put this hypothesis to experimental test. If the ThX is removed from the thorium as soon as it is formed over a sufficient period, the former will be prevented from

exciting activity on the latter, and that already excited will decay spontaneously. The experiment was therefore performed. A quantity of nitrate was precipitated as hydroxide in the usual way to remove ThX, the precipitate redissolved in nitric acid, and again precipitated after a certain interval. From time to time a portion of the hydroxide was removed and its radioactivity tested. In this way the thorium was precipitated in all 23 times in a period of 9 days, and the radioactivity reduced to a constant minimum. The following table shows the results:—

	Activity of Hydroxide. per cent.
After first precipitation	46
After precipitations at three intervals of 24 hours	39
At three more intervals each of 24 hours, and three more each of 8 hours	22
At three more each of 8 hours	24
At six more each of 4 hours	25

The constant minimum thus attained—about 25 per cent. of the original activity—is thus about 21 per cent. below that obtained by two successive precipitations without interval, which has been shown to remove all the ThX separable by the process. The rate of recovery of this 23 times precipitated hydroxide was then measured (fig. 4). It will be

Fig. 4.



seen that it is now quite normal, and the initial drop characteristic of the ordinary curve is quite absent. It is in

fact almost identical with the ordinary curve (fig. 2) that has been produced back to cut the vertical axis, and there is thus no doubt that there is a residual activity of thorium unconnected apparently with ThX, and constituting about one fourth of the whole.

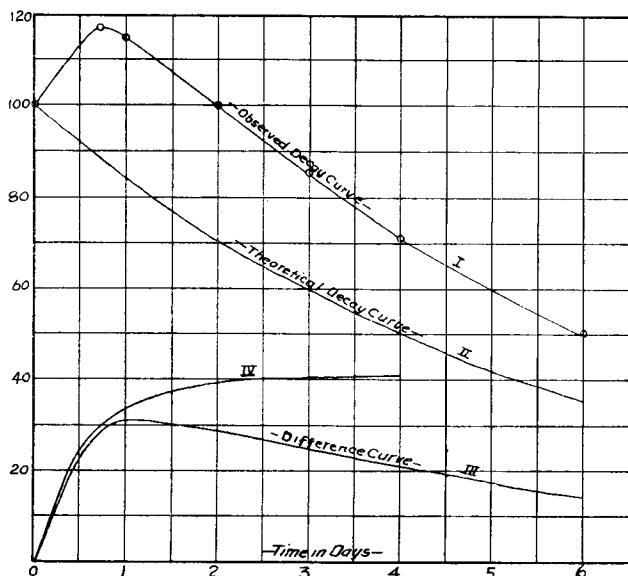
The decay-curves of several of the fractions of ThX separated in this experiment after varying intervals of time were taken for the first few days. All of them showed the initial rise of about 15 per cent. at the end of 18 hours, and then a normal decay to zero. The position is thus proved that the initial irregularities are caused by the secondary radiation excited by ThX upon the surrounding matter. By suitably choosing the conditions the recovery-curve can be made to rise normally from a constant minimum, and the decay-curve be shown to consist of two curves, the first the rate of production of excited radioactivity, and the second the rate of decay of the activity as a whole.

So far nothing has been stated as to whether the excited radioactivity which contributes about 21 per cent. of the total activity of thorium is the same or different from the known type produced by the thorium emanation. All that has been assumed is that it should follow the same general law; *i. e.* the effect will increase with the time of action of the exciting cause, and decrease with time after the cause is removed. If the rate of rise of the excited activity be worked out from the curves given (fig. 5) it will be found to agree with that of the ordinary excited activity, *i. e.* it rises to half value in about 12 hours. Curve 1 is the observed decay-curve for ThX; curve 2 is the theoretical curve, assuming that it decreases geometrically with time and falls to half value in four days. Curve 3 is obtained by plotting the difference between these two, and therefore constitutes the curve of excited activity. Curve 4 is the experimental curve obtained for the rise of the excited radioactivity from the thorium emanation when the exciting cause is constant. But the exciting cause (ThX) in the present case is not constant, but is itself falling to half value in 4 days, and hence the difference curve, at first almost on the other, drops away from it as time goes on, and finally decays to zero. There is thus no reason to doubt that the effect is the same as that produced by the thorium emanation, which is itself a secondary effect of ThX. Curve 3 (fig. 2) represents a similar difference curve for *the decay* of excited activity, plotted from *the recovery curve* of thorium.

Since this effect of excited activity is caused by the emanation, it seemed reasonable to suppose that it will be greater, the

less the emanation succeeds in escaping in the radioactive state, and therefore that de-emanated compounds should

Fig. 5.



possess a greater proportion of excited radioactivity than those with high emanating power. This conclusion was tested by converting a specimen of thorium carbonate with an emanating power five times that of ordinary thoria, into oxide and de-emanating by intense ignition. The energy that before escaped in the form of emanation is now, all but a few per cent., prevented from escaping. The radioactivity of the oxide so prepared rose in the first three days about thirty per cent. of its original amount, and there thus seem to be grounds for the view that the excited radioactivity will contribute a much greater effect in a non-emanating thorium compound than in one possessing great emanating power.

Additional confirmation of this view is to be found in the nature of the radiations emitted by the two classes of compounds (Section XI.).

X. *The Non-separable Radioactivity of Thorium.*

It has not yet been found possible by any means to free thorium from its residual activity, and the place of this part in the scheme of radioactivity of thorium remains to be considered. Disregarding the view that it is a separate

phenomenon, and not connected with the major part of the activity, two hypotheses can be brought forward capable of experimental test, and in accordance with the views advanced on the nature of radioactivity, to account for the existence of this part. First, if there was a second type of excited activity produced by ThX similar to that known, but with a very slow rate of decay, it would account for the existence of the non-separable activity. If this is true it will not be found possible to free thorium from this activity by chemical means, but the continuous removal of ThX over a very long period would, as in the above case, cause its spontaneous decay.

Secondly, if the change which gives rise to ThX produces a second type of matter at the same time, *i. e.* if it is of the type of a decomposition rather than a depolymerization, the second type would also in all probability be radioactive, and would cause the residual activity. On this view the second type of matter should also be amenable to separation by chemical means, although it is certain from the failure of the methods already tried that it resembles thorium much more closely than ThX. But until it is separated from the thorium producing it, its activity will not decay spontaneously. Thus what has already been shown to hold for ThX will be true for the second constituent if methods are found to remove it from the thorium.

It has been shown (Soddy, *loc. cit.*) that uranium also possesses a non-separable radioactivity extremely analogous to that possessed by thorium, and whatever view is taken of the one will in all probability hold also for the other. This consideration makes the second hypothesis, that the residual activity is caused by a second non-thorium type of matter produced in the original change, the more probable of the two.

XI. *The Nature of the Radiations from Thorium and ThX.*

From the view of radioactivity put forward it necessarily follows that the total radioactivity of thorium is altered neither in character nor amount by chemical treatment. With regard to the first, the amount of activity, it has been pointed out that the intensity of radiations *emitted* do not furnish alone a measure of the activity. The absorption in the mass of material must be considered also. The radiations of thorium oxide are derived from a very dense powder; those from ThX, on the other hand, have only to penetrate a very thin film of material. The difficulty can be overcome to some extent by taking for the comparison the radioactivity of a thin film of a soluble thorium salt produced by evaporating

a solution to dryness over a large metal plate. Compared in this way, the radioactivity of ThX when first separated almost exactly equals the activity of the nitrate from which it is produced, while the hydroxide retains about two-fifths of this amount. The total activity of the products is therefore greater than that of the original salt; but this is to be expected, for it is certain that more absorption takes place in the nitrate than in the products into which it is separated.

Similar difficulties stand in the way of an answer to the second question, whether the nature of the radiations is affected by chemical treatment, for it has been experimentally observed that the penetrating power of these radiations decreases with the thickness of material traversed. The character of the radiations from ThX and thorium have, however, been compared by the method of penetration power. A large number of comparisons justifies the view that the character of thorium radioactivity is unaltered by chemical treatment and the separation of ThX, although the different types are unequally distributed among the separated products.

Determinations of the proportion of rays deviable by the magnetic field in thorium and ThX throws fresh light on the question. The general result is that ThX gives out both deviable and non-deviable rays, and the same applies to the excited activity produced by ThX. But in the experiment in which the excited radiation was allowed to spontaneously decay, by removing ThX as formed, the thorium compound obtained after 23 precipitations was found to be quite free from deviable radiation. This is one of the most striking resemblances between the non-separable radioactivities of uranium and thorium, and warrants the question whether the primary radiation of ThX is not, like that of UrX, composed entirely of cathode-rays. There is, however, no means of deciding this point owing to the excited radiation which always accompanies the primary radiation of ThX, and which itself comprises both types of rays.

Finally, it may be mentioned that the proportion of deviable and non-deviable radiation is different for different compounds of thorium. The nitrate and ignited oxide, compounds which hardly possess any emanating power, have a higher proportion of deviable radiation than compounds with great emanating power. This is indirect evidence of the correctness of the view already put forward (Section IX.), that when the emanation is prevented from escaping it augments the proportion of excited radioactivity of the compound.

XII. *Summary of Results.*

The foregoing experimental results may be briefly summarized. The major part of the radioactivity of thorium—ordinarily about 54 per cent.—is due to a non-thorium type of matter, ThX, possessing distinct chemical properties, which is temporarily radioactive, its activity falling to half value in about four days. The constant radioactivity of thorium is maintained by the production of this material at a constant rate. Both the rate of production of the new material and the rate of decay of its activity appear to be independent of the physical and chemical condition of the system.

The ThX further possesses the property of exciting radioactivity on surrounding inactive matter, and about 21 per cent. of the total activity under ordinary circumstances is derived from this source. Its rate of decay and other considerations make it appear probable that it is the same as the excited radioactivity produced by the thorium emanation, which is in turn produced by ThX. There is evidence that, if from any cause the emanation is prevented from escaping in the radioactive state, the energy of its radiation goes to augment the proportion of excited radioactivity in the compound.

Thorium can be freed by suitable means from both ThX and the excited radioactivity which the latter produces, and then possesses an activity about 25 per cent. of its original value, below which it has not been reduced. This residual radiation consists entirely of rays non-deviable by the magnetic field, whereas the other two components comprise both deviable and non-deviable radiation. Most probably this residual activity is caused by a second non-thorium type of matter produced in the same change as ThX, and it should therefore prove possible to separate it by chemical methods.

XIII. *General Theoretical Considerations.*

Turning from the experimental results to their theoretical interpretation, it is necessary to first consider the generally accepted view of the nature of radioactivity. It is well established that this property is the function of the atom and not of the molecule. Uranium and thorium, to take the most definite cases, possess the property in whatever molecular condition they occur, and the former also in the elementary state. So far as the radioactivity of different compounds of different density and states of division can be compared together, the intensity of the radiation appears to depend only on the quantity of active element present. It

is not at all dependent on the source from which the element is derived, or the process of purification to which it has been subjected, provided sufficient time is allowed for the equilibrium point to be reached. It is not possible to explain the phenomena by the existence of impurities associated with the radioactive elements, even if any advantage could be derived from the assumption. For these impurities must necessarily be present always to the same extent in different specimens derived from the most widely different sources, and, moreover, they must persist *in unaltered amount* after the most refined processes of purification. This is contrary to the accepted meaning of the term impurity.

All the most prominent workers in this subject are agreed in considering radioactivity an atomic phenomenon. M. and Mme. Curie, the pioneers in the chemistry of the subject, have recently put forward their views (*Comptes Rendus*, cxxxiv. 1902, p. 85). They state that this idea underlies their whole work from the beginning and created their methods of research. M. Becquerel, the original discoverer of the property for uranium, in his announcement of the recovery of the activity of the same element after the active constituent had been removed by chemical treatment, points out the significance of the fact that uranium is giving out cathode-rays. These, according to the hypothesis of Sir William Crookes and Prof. J. J. Thomson, are *material* particles of mass one thousandth of the hydrogen atom.

Since, therefore, radioactivity is at once an atomic phenomenon and accompanied by chemical changes in which new types of matter are produced, these changes must be occurring within the atom, and the radioactive elements must be undergoing spontaneous transformation. The results that have so far been obtained, which indicate that the velocity of this reaction is unaffected by the conditions, makes it clear that the changes in question are different in character from any that have been before dealt with in chemistry. It is apparent that we are dealing with phenomena outside the sphere of known atomic forces. Radioactivity may therefore be considered as a manifestation of subatomic chemical change.

The changes brought to knowledge by radioactivity, although undeniably material and chemical in nature, are of a different order of magnitude from any that have before been dealt with in chemistry. The course of the production of new matter which can be recognized by the electrometer, by means of the property of radioactivity, after the lapse of a few hours or even minutes, might conceivably require geological epochs to attain to quantities recognized by the

balance. However the well-defined chemical properties of both ThX and UrX are not in accordance with the view that the actual amounts involved are of this extreme order of minuteness. On the other hand, the existence of radioactive elements at all in the earth's crust is an *à priori* argument against the magnitude of the change being anything but small.

Radioactivity as a new property of matter capable of exact quantitative determination thus possesses an interest apart from the peculiar properties and powers which the radiations themselves exhibit. Mme. Curie, who isolated from pitchblende a new substance, radium, which possessed distinct chemical properties and spectroscopic lines, used the property as a means of chemical analysis. An exact parallel is to be found in Bunsen's discovery and separation of caesium and rubidium by means of the spectroscope.

The present results show that radioactivity can also be used to follow *chemical changes occurring in matter*. The properties of matter that fulfil the necessary conditions for the study of chemical change without disturbance to the reacting system are few in number. It seems not unreasonable to hope, in the light of the foregoing results, that radioactivity, being such a property, affords the means of obtaining information of the processes occurring within the chemical atom, in the same way as the rotation of the plane of polarization and other physical properties have been used in chemistry for the investigation of the course of molecular change.

Macdonald Physics Building,
Macdonald Chemistry and Mining Building,
McGill University, Montreal.

XLII. *On a Remarkable Case of Uneven Distribution of Light in a Diffraction Grating Spectrum.* By R. W. WOOD, Professor of Experimental Physics, Johns Hopkins University*.

IT is a well-known fact that in the spectra formed by a diffraction-grating the light is unevenly distributed, that is the total light in any one spectrum will not recombine to form white light.

I have been examining a most remarkable grating recently ruled on one of the Rowland dividing-engines in which this uneven distribution is carried to a degree almost incomprehensible. If the spectra of an incandescent lamp are viewed directly in the grating without any other optical appliance, at certain angles of incidence perfectly sharp monochromatic

* Communicated by the Physical Society: read June 20, 1902.