LXXXIV.—*The Radioactivity of Thorium Compounds.*
II.   The Cause and Nature of Radioactivity.

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AT the close of the first paper on this subject (this vol., p. 321), it was shown that a constituent responsible for part of the radioactivity of thorium could be separated from its compounds by chemical means. Two methods were given.   In one, a thorium solution was precipitated by ammonia, and the thorium hydroxide precipitate showed only about one-third of the normal activity, whilst the filtrate, on evaporation and removal of the ammonium salts by ignition, left a very active residue —in some cases more than a thousand times as active as an equal weight of thoria.   In the other method, thorium oxide was washed repeatedly with large quantities of water.   The washings, on evaporation, deposited very active residues, whilst the radioactivity of the thoria was appreciably diminished by the process.

In both these methods, the active residues are extremely small, and the view was put forward that even the most active specimens consisted largely of accidental impurities, ThX, the active constituent of thorium, being only present in minute amount.   By the kindness of Dr. Knöfler, of Berlin, who in the friendliest manner placed at our disposal a large specimen of his purest thorium nitrate, we were at once able to confirm this opinion.   This specimen, which had been purified by many processes, did not contain any of the impurity precipitable by sodium phosphate after the removal of the thorium with ammonia, which was present in the commercial nitrate previously used. The radioactivity and emanating power of Dr. Knöfler's specimen were, however, at least as great as any other in our possession, and the residues obtained from the filtrate after precipitating with ammonia were no less active.

I. *Scope of the Present Paper.*

In the present communication, the results of a further detailed investigation of the radioactivity and emanating power of thorium compounds are given, and these have led to a theoretical interpretation of the processes involved which give rise to the phenomenon of natural radioactivity.

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 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 (*Compt. rend.*, 1901, **133**, 977) 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.

II. *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 0·5 gram was left undisturbed throughout the whole series of measurements on the plate over which it had been

sifted, and was compared always with 0·5 gram of ordinary de-eman-
ated thorium hydroxide 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 rate of increase of emanating power of the same preparation
was determined at the same time (see section VII).   The methods and
apparatus employed have been described in the previous paper.

The active filtrate from the preparation was concentrated and made
up to 100 c.c. in volume.   One-fourth was evaporated to dryness, the
ammonium nitrate expelled by ignition in a platinum dish, and the
radioactivity of the residue tested at the same intervals as the hydr-
oxide to determine the rate of decay of its activity. The comparison in
this case was made with 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 (sections V and VII).

The following table gives an example of one of a numerous series
of observations made with different preparations at different times.
The maximum value attained 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. 1 (p. 840) 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 diminished, and had about the same value after two days

3 к 2

as when first prepared.   The activity of the ThX, on the other hand,
at first increases, and does not begin to fall below its original value
until after the lapse of two days (compare section VIII).   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

FIG. 1.

Time in days.
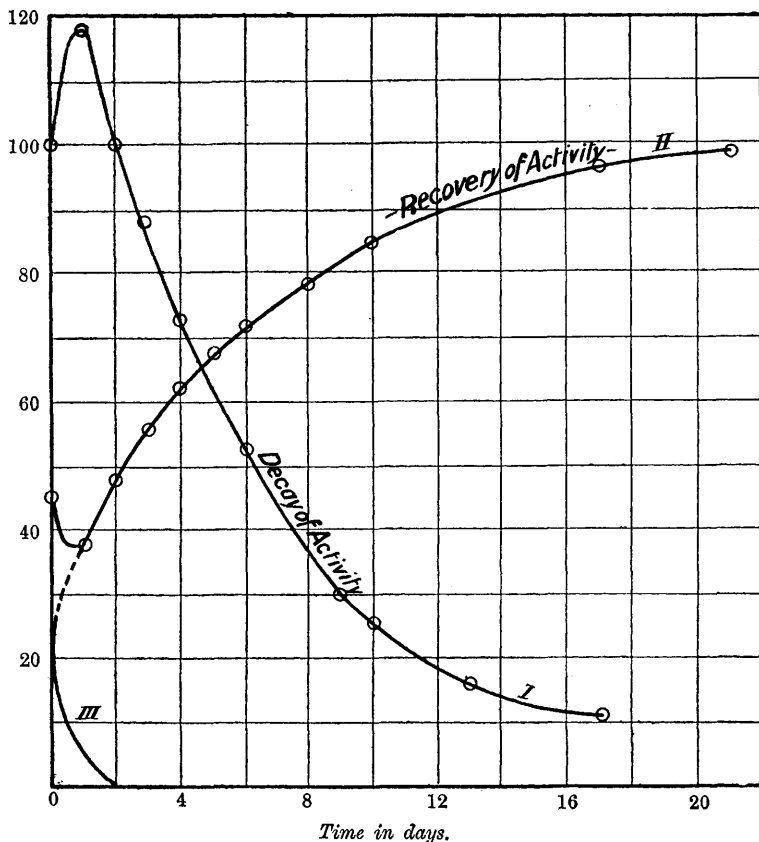
method of washing decayed very similarly to that of ThX, as shown
by the above curve.

If for present purposes the initial periods of the curve are dis-
regarded and the latter 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, namely, 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 (fig 4, p. 853). This is brought out by figure 2, which represents the recovery curve

Fig. 2.

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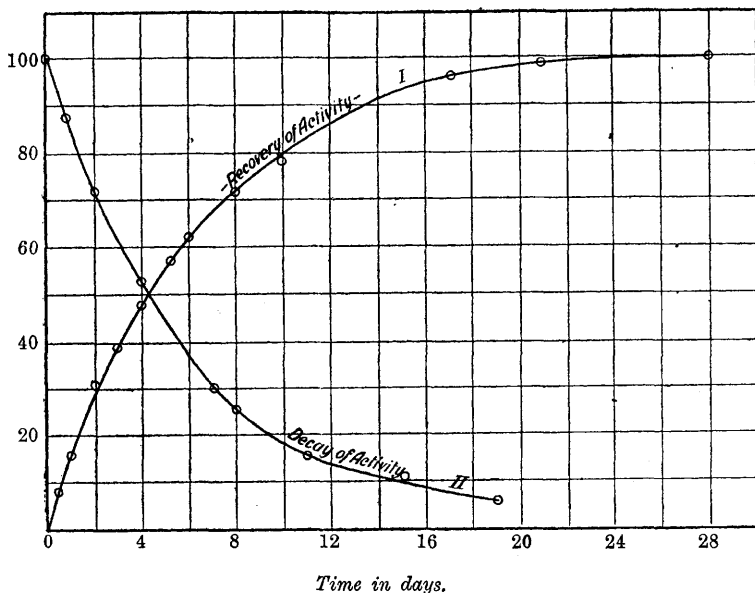
in which the percentage amounts of activity recovered, reckoned from this 25 per cent. minimum, are plotted as ordinates. In the same figure, the decay curve after the second day is shown on the same scale.

The activity of ThX decreases very approximately in a geometrical progression with the time, that is, if I_0 represent the initial activity, and I_t the activity after time t

$$\frac{I_t}{I_0} = e^{-\lambda t} \qquad . \quad . \quad . \quad . \quad . \quad (1)$$

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 there-
fore be approximately expressed by the equation

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

where I_0 represents the amount of activity recovered when the maxi-
mum 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 (Rutherford,
Phil. Mag., 1900, [v], **49**, 10, 181) to express the rise of activity to a
constant maximum of a system consisting of radiating particles in
which

(i). The rate of supply of fresh radiating particles is constant,

(ii). 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 radio-
activity 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 continu-
ously produced.

III. *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 in the residue remaining.

This view, however, can be shown to be quite untenable, for according
to 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, after evaporation and ignition, is free from activity, and the thorium carbonate obtained 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 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 obtained by Sir William Crookes with uranium, which we have confirmed by the electrical method, may here be mentioned. UrX is completely precipitated by ammonia together with the 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.

IV. *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 precipitation in hot dilute solutions by dilute ammonia is the most favourable condition for the separation. Five grams of thorium nitrate, as obtained from the maker, were 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 a measurement of the activity of the residues obtained from the successive filtrates. The activity of the ThX from the first filtrate was equivalent to that of 4·23 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 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 which 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 that of 8·3 grams of thorium oxide. This experiment was performed on the same day as the one recorded above, in which 5 grams of the new sample of nitrate had been employed, and it will be seen that there is no difference in the activity of the filtrates in the two cases. In one month, the activity of the ThX in a thorium compound again reaches 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 these 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 diminution of the activity of the product in geometrical progression with the time.

By using the Dolezalek electrometer, on which the radioactivity of 1 mg. of thoria produces a measurable effect, 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 elapse, 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 0·01 and 0·02 microfarad, which reduce the sensitiveness to less than one-hundredth and one two-hundredth of the normal, were frequently employed in dealing with these active residues. For ordinary work with 0·25 to 0·5 gram of thorium compound, 0·001 microfarad was necessary. Most of the measurements in the course of the present paper were made with this instrument, and a range from that represented by 1 milligram of thoria to any desired maximum could readily be obtained. Of course, the greatest care is necessary in working with so sensitive an instrument to prevent electrostatic disturbances of every kind.

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 VIII), after twenty-three successive precipitations extending over 9 days, the amount formed during the last interval was, so far as

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could be judged, no less than that produced at the beginning of the process.

The phenomenon of radioactivity, by the aid 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 to take place.

V. *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 effect of conditions upon its rate of production.

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 first be found. It was observed that, like all other types of temporary radioactivity, the rate of decay is not altered by any known agency. It is not affected by ignition or chemical treatment, and the material responsible for it can be dissolved in acids and reobtained 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. 1) was allowed to stand, and at the end of 12 days a second fourth part was evaporated to dryness and ignited, and its activity compared with that of the first, which had been left since evaporation in 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 fourth part was evaporated, and the activity, now very small, was indistinguishable from that of the fraction first evaporated. Resolution of the residue after the activity had decayed does not regenerate it. The activity of ThX thus decays at a rate independent of the chemical and physical condition of the molecule.

The rate of recovery of activity under different conditions in thorium compounds therefore 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 over the blow-pipe 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 VIII) 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 that this is the case.

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 week following the 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 of the treatment. 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 VII, 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 rates of recovery and decay of
activity in uranium 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.

VI. *The Cause and Nature of Radioactivity.*

The foregoing conclusions enable a generalisation 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 ele-
ments, to take the best established cases, thorium, uranium, and
radium. In their first paper on the present subject, the authors
showed that the radioactivity of the emanation produced by thorium
compounds decayed geometrically with the time under all conditions,
and was not affected by the most drastic chemical and physical treat-
ment. The same has been shown by one of us (Rutherford, *Phil.
Mag.*, 1900, [v], 49, 161) to hold for the excited radioactivity pro-
duced 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 to account for this.

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, behaves in
the same way as the other typically radioactive substances 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 of 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 substance 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 into the same category.

VII. *The Place of Emanating Power in the Radioactivity of Thorium.*

Turning from radioactive solids to gases which manifest this property, many of the very puzzling results obtained in the investigation of the radioactive emanation produced by thorium compounds can now also be simply explained. This section is devoted to the purpose and to further work which has been carried out in order to determine more exactly the place of emanating power in the radioactivity of thorium.

It was shown that the solutions from which thorium hydroxide had been precipitated by ammonia possessed about as much emanating power as the solutions from which they were prepared, whilst the precipitated hydroxide in all cases but one was more or less completely de-emanated, but spontaneously regained its normal value with lapse of time. In one solitary instance that could not be repeated (this vol., p. 344) the hydroxide had an abnormally *high* emanating power, decaying to nearly normal value in 14 days ; this can now be explained. The thorium was first partly precipitated as thorium carbonate by means of sodium carbonate, and nitric acid added to redissolve a part. Under these circumstances, all the ThX remained in solution, and on adding ammonia the thorium only should be precipitated, which, as always occurred when the experiment was repeated, ought to be more or less free from emanating power. But if, as apparently happened in this case, care was not taken to boil off all the carbon dioxide produced before adding ammonia, the latter would re-form a carbonate which completely precipitated both ThX and thorium. Hence the small hydroxide fraction contained all the ThX originally present, and possessed a high emanating power decaying to normal value with time. The fact that the carbonate fraction in this same experiment behaved abnormally and did *not* recover its emanating power is more difficult to explain and the point will be reverted to later.

In further explanation of the results then obtained it is only necessary to point out that since emanating power and not radioactivity was the first object of the investigation, any measurements of the latter, especially in the earlier part of the paper, were, as a rule, performed long after the specimens had been prepared, that is, after they had regained their normal values. In some cases, if these measurements had been

made immediately after preparation the results would have doubtless been different.

The conclusion was arrived at that emanating power was the manifestation of a dynamical change of the nature of a chemical reaction rather than a function of matter in the static state, even before it was known that the emanating material ThX was being continuously reproduced. The latter discovery, however, enables a fairly complete explanation of the phenomenon to be given.

On resuming the work after the Christmas vacation, it was found on the one hand that some concentrated filtrates possessing high emanating power originally had completely lost it with lapse of time, and on the other, that the emanating power of almost all of the numerous samples of thorium hydroxide and carbonate prepared had regained about the same value, namely, between three and four times that of thorium oxide. The rate of decay of the emanating power of ThX and the recovery of this property by the thorium from which it had been separated were then investigated in parallel with the similar experiments on radioactivity already described. One-fourth of the concentrated filtrate used for the latter purpose was taken, and the decrease of its emanating power with time measured. The increase of emanating power of the thorium hydroxide from which it had been prepared was also measured. The curves (Fig. 3, p. 850) express the results. The decay curve is merely approximate, for it is not easy to determine accurately the emanating power of a liquid without special arrangements to ensure the constancy of the air current and the shaking of the solution. The experiments, although merely approximate, bear out the conclusion that emanating power decays and recovers according to the same law as the radioactivity of ThX, and that it is therefore one of the properties of the latter and not of thorium. If care be taken to remove the ThX, the thorium almost entirely loses its emanating power. The small fraction that remains, often only a few per cent. of the maximum, can be accounted for by the reproduction of ThX during the time taken to dry the precipitate. The decay curve given, so far as it can be relied on, shows that the emanating power of ThX at any instant is proportional to its radioactivity.

It was shown in the first paper that the emanation consisted of a chemically inert gas continuously emitted from thorium compounds. The results therefore find their simplest expression on the view that just as a chemical change is proceeding in thorium whereby a non-thorium material is produced, so the latter undergoes a further transformation, giving rise to a gaseous product which in the radioactive state constitutes the emanation.

It will be seen at once that this secondary change is of a different kind from the primary, for it is affected apparently by the conditions

in a very marked manner. It was shown that moisture, the state of aggregation, and temperature influenced the value of emanating power. From $-80°$ to a red heat, the latter regularly increases in the ratio of $1 : 40$ in the case of thorium oxide, whilst the ratio between the values for thorium nitrate in the solid state and in solution is as $1 : 200$. The secondary reaction appears therefore at first sight much more nearly allied to ordinary chemical reaction than the primary. It must not be forgotten, however, that the laws controlling the manifestation of the two phenomena, radioactivity and emanating power, are of necessity very different. In the former, we deal with the intensity of radiations

FIG. 3.

Time in days.
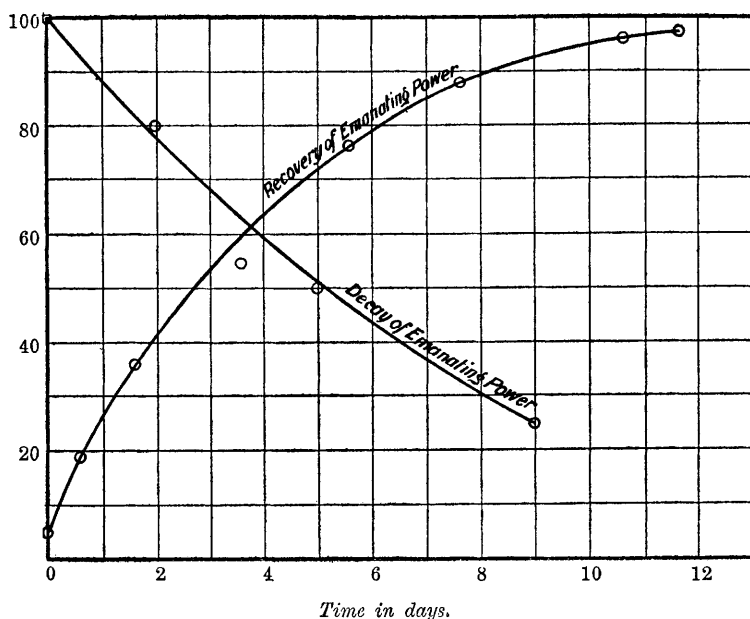
emitted by a solid, in the latter with the rate of escape of a gas into the surrounding air from either a solid or a liquid. Since this gas is detected by its radioactivity, and this decays extremely rapidly with time, a very slight delay in the rate of its escape will enormously affect the experimental value obtained for emanating power. It is possible that this cause is sufficient to account for the results obtained at different temperatures and with solids and liquids. De-emanation by ignition, on this view, would mean that at a certain temperature the crystalline form of thoria is permanently altered in such a way that the emanation is delayed in its escape.

On the other hand, it is now well established by experiment that sometimes thorium compounds de-emanated chemically by removal of ThX do not recover their normal emanating power with time, but remain constant at a lower value. The carbonate mentioned in the last paper and already referred to is an example of this, for it possessed hardly any emanating power until it was again dissolved and precipitated. On one occasion, two samples of hydroxide, prepared from different nitrates, were tested together for rise of emanating power. That of the one rose normally to its maximum (as in Fig. 3), which was twenty times the minimum. The other started from the same minimum, but rose to a maximum only one-fourth as great. When the experiment was repeated under the same conditions, using the same sample of nitrate, the compound behaved normally. It thus appears that the emanation can be almost entirely prevented from escaping in the radioactive state in some cases, and partially prevented in others where no visible peculiarity of physical condition exists and where other preparations similarly prepared behave normally.

The question is further complicated by the property possessed by the emanation of exciting radioactivity on *all* surfaces with which it comes into contact. This process must be going on in the matter of the thorium compound itself, and it will be shown (section VIII) that this effect contributes an important quota to the total radioactivity of the compound. It seemed reasonable to suppose that the effect will be the greater the less the extent to which emanation succeeds in escaping in the radioactive state, and therefore that de-emanated compounds should 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 it 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 oxides so prepared rose in the first three days to about 30 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 having 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 X).

It will be seen that the phenomenon is too complicated to allow of an answer at the present stage to the question whether the secondary change which produces the emanation is, like the primary, independent of the conditions or not.

VIII. *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 remains after the removal of ThX.

A study of the curves (Fig. 1) shows that in each case a double action is probably at work. It must be supposed that the normal decay and recovery are taking place, but are being masked by a simultaneous rise and decay from causes unknown. From what is known of the radioactivity of thorium, it was surmised that an action might be taking place similar to that effected by the emanation of exciting radioactivity on surrounding inactive matter. On this view, the residual activity of thorium might consist in whole or 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.

After precipitations:

At three intervals of 24 hours......................	39 per cent.
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 an interval, which has been shown to remove all the ThX separable by the process. The rate of recovery of this hydroxide precipitated 23 times was then measured (Fig. 4). It will be seen that it is now quite normal and the initial drop characteristic of the ordinary curve is absent. It is, in fact, almost identical with the ordinary curve (Fig. 1) produced back to cut the

Fig. 4.

Time in days.
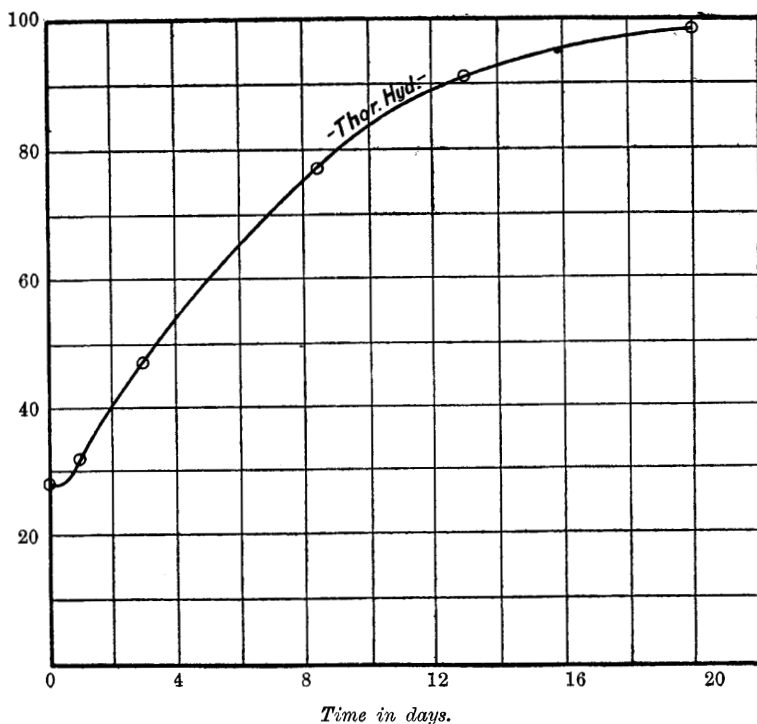
vertical axis, and there is thus no doubt that there is a residual activity of thorium unconnected apparently with ThX, and constituting about one-fourth of the whole.

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. It is a significant fact that exactly similar curves have already been obtained by one of us (*Phys. Zeit.*, 1902, 3, 254) for the excited radioactivity produced by the thorium emanation under very similar conditions. If a negatively charged wire be exposed *for a few minutes only* to the thorium emanation, the excited radioactivity produced at first increases to several times its value for the first few hours after the exciting cause is removed, and then commences to decay, exactly as in the case of ThX.

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, that is, the effect should increase with the time of action of the exciting cause, and decrease with time after the cause is removed. If the rate of increase 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, that is, it rises to half the value in about 12 hours. Curve I is the observed decay curve for ThX, curve II is the theoretical curve, assuming that it decreases geometrically with the time and falls to half value in four days. Curve III is obtained by plotting the difference between these two, and therefore constitutes the curve of excited activity. Curve IV 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. Curve III, Fig. 1, represents a similar difference curve for *the decay* of excited activity, plotted from *the recovery curve* of thorium. 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.

IX. *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.

FIG. 5.

Time in days.
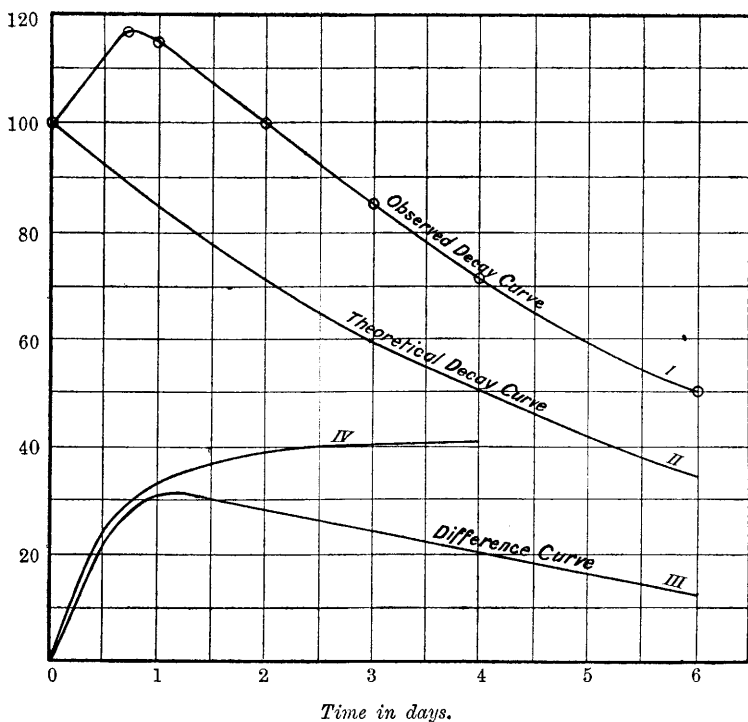
Secondly, if the change which gives rise to ThX produces a second type of matter at the same time, that is, if it is of the type of a decomposition rather than a depolymerisation, the second type would also in all probability be radioactive, and would cause the residual activity. On this view, the second 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

3 L 2

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 is shown in the following communication by one of us (p. 860) 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.

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

It has recently been found (Rutherford and Grier, *Phys. Zeit.*, 1902, 3, 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.

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. This conclusion can be tested by comparing the radiations of thorium and ThX with the mixture which constitutes the thorium radiation. It must, however, be pointed out that it is difficult to make any absolute measurement of radioactivity on account of the different extents in different cases to which the radiations are absorbed in the material of the substance emitting them. The total radioactivity of the original thorium is derived from a small quantity of the substance in the form of powder, whilst the radiations from ThX are produced by a very thin film of the material on the platinum dish. The radiation from thorium is absorbed to the extent of one-half by aluminium foil 0.0004 cm. thick, and as thorium oxide is far denser than aluminium, it is probable that the radiation in this case is confined to a surface layer only 0.0001 cm. deep. In the ThX, on the other hand, there is probably but little absorbed in the substance itself. 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 is almost exactly equal to the activity of the nitrate from which it is produced, whilst the hydroxide retains about two-fifths of this amount. The difference is in the

expected direction, for it is certain that more absorption takes place
in the nitrate than in the products into which it is separated. The
requirements of the hypothesis can thus be said to be satisfied, but the
example illustrates the difficulty of making absolute measurements of
radioactivity. These throughout have almost completely been avoided.
It is possible to trace with great accuracy the *change* of radioactivity
of any preparation by leaving it undisturbed on its original plate and
comparing it always with the same comparison sample ; but to express
the radioactivity of one body like ThX in terms of that of another like
thoria, except for the purposes of comparison, is misleading, as the
above consideration shows.

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 observed experimentally that the penetrative
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 penetrative 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 dis-
tributed among the separated products.

The determination of the proportion between the deviable and non-
deviable rays affords a new means of approaching the question. The
general result is that the radiations from ThX and the excited radia-
tion it produces both comprise deviable and non-deviable radiation.
But in the experiment in which the excited radiation was allowed to
decay spontaneously by removing the ThX as formed, the final pro-
duct, after 23 precipitations, was found to be quite free from deviable
radiation. This, as will be shown in the following paper, is one of the
most striking resemblances between the non-separable radioactivities
of uranium and thorium.

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 VII), that when
the emanation is prevented from escaping it augments the proportion
of excited radioactivity of the compound.

XI. *Summary of Results.*

The foregoing experimental results may be briefly summarised.
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 the 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 is undergoing a further change, and one of the products is gaseous and in the radioactive state constitutes the emanation produced by thorium compounds. 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 probable that it is the same as the excited radioactivity produced by the thorium emanation, which has been shown to be produced by ThX. There is evidence that if by any means 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 the ThX, and it should therefore prove possible to separate it by chemical methods.

XII. *General Theoretical Considerations.*

Turning from the experimental results to their theoretical interpretation, it is necessary first to 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 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 stated (*Compt. rend.*, 1902, **134**, 85) 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 Professor J. J. Thomson, are *material* particles of mass one-thousandth that of the hydrogen atom.

The present researches had as their starting point the facts that had come to light with regard to the emanation produced by thorium compounds and the property it possesses of exciting radioactivity on surrounding objects. In each case, the radioactivity appeared as the manifestation of *a special kind of matter* in minute amount. The emanation behaved in all respects like a gas, and the excited radioactivity it produces as an invisible deposit of intensely active material independent of the nature of the substance on which it was deposited, and capable of being removed by rubbing or the action of acids.

The position is thus reached that radioactivity is at once an atomic phenomenon and the accompaniment of a chemical change in which new kinds of matter are produced. The two considerations force us to the conclusion that radioactivity is a manifestation of sub-atomic chemical change.

There is not the least evidence for assuming that uranium and thorium are not as homogeneous as any other chemical element, in the ordinary sense of the word, so far as the action of *known* forces is concerned. The idea of the chemical atom in certain cases spontaneously breaking up with evolution of energy is not of itself contrary to anything that is known of the properties of atoms, for the causes that bring about the disruption are not among those that are yet under our control, whereas the universally accepted idea of the stability of the chemical atom is based solely on the knowledge we possess of the forces at our disposal.

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 recognised by the electrometer, by means of the property of radioactivity, after the course of a few hours or even minutes, might possibly require geological epochs to attain to quantities recognised by the balance. It is true that 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, yet, on the other hand, the existence of radioactive elements at all in the earth's crust is an *a priori* argument against the magnitude of the change being anything but small.

It is a significant fact that the radioactive elements are all at the end of the periodic table. If we suppose that radium is the missing second higher homologue of barium, then the known examples— uranium, thorium, radium, polonium (bismuth), and lead are the five elements of heaviest atomic weight. Nothing can yet be stated of the mechanism of the changes involved, but whatever view is ultimately adopted it seems not unreasonable to hope that radioactivity affords the means of obtaining information of processes occurring within the chemical atom.

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