APPENDIX

RADIUM, AND RADIOACTIVE ELEMENTS

AS far back as the year 1896, Becquerel discovered that the element uranium and its salts possess the remarkable property of emitting rays somewhat similar in character to the now familiar Röntgen or "X" rays; resembling these rays in their penetrating power, their photographic action, and their action upon electrified gases. These peculiar rays were distinguished from the Röntgen rays by being called the "uranium," or the "Becquerel" rays. Somewhat later it was found that the element thorium and its compounds were likewise possessed of the property of emitting rays, which, while differing from both the "X" and the "uranium" rays in some respects, closely resembled them in others. To denote this property, the term *radioactivity* has been coined, and substances possessing the property are said to be *radioactive* bodies.

In 1898 it was announced that M. and Mme. Curie had discovered a new radioactive substance contained in *pitchblende*, a mineral consisting essentially of uranium oxide. From researches already made, it had been shown that the radioactivity of uranium compounds is roughly proportional to the amount of the metal present, but it was found that in the case of certain specimens of pitchblende this was not the case, but that the radioactivity was greatly in excess of that calculated from the percentage of uranium in the mineral. This fact suggested the presence of some new substance of superior radioactivity to that possessed by uranium. It was found in the ordinary process of separation of the metals by precipitation from an acid solution by sulphuretted hydrogen, that this new active substance was thrown down along with the sulphides, and finally was separated from the copper and arsenic, &c., and remained associated with the bismuth. No isolation of the new substance was effected, but from its greatly superior radioactivity the discoverers concluded that there was sufficient evidence of the presence of a new element to warrant them in giving it a name. They therefore called it *polonium*, from the country from which the pitchblende was obtained.* (*Compt. rend.* 127, p. 175.)

Following up their investigations, the same workers very shortly afterwards discovered in the same mineral another radioactive body of still far greater activity. This new substance, they found, is not precipitated by either sulphuretted hydrogen, ammonium sulphide, or ammonia, but is associated

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* Although the name *polonium* is still met with in the literature of the subject, no further evidence has been produced in proof of the existence of a new element corresponding to the name. The name is used rather to denote the radioactivity which appears to be associated with the element bismuth.

with and accompanies barium in the various chemical reactions the latter element undergoes. Thus, when barium sulphate or carbonate is precipitated from a solution of the chloride, the precipitated barium compound is accompanied by the radioactive material; or when the chloride itself is precipitated either by strong hydrochloric acid or by alcohol, the "active" substance is thrown down along with it.

By the careful fractional precipitation of the chloride with alcohol it was found possible to gradually concentrate the radioactive substance in the barium chloride, and in this way a product was obtained possessing a radioactivity 900 times greater than that of uranium. In view of the intensity of its "activity," the discoverers gave the name *radium* to the new element which they believed to be present, although in almost infinitely minute quantities. (*Compt. rend.* 127, p. 1215.)

The spectrum exhibited by this "active" barium chloride also confirmed the presence of a new element, for besides the lines belonging to barium it contained a well-defined line which had never previously been observed in the spectra of any of the known elements.

Determinations of the atomic weight of the metal (barium) in the specimens of barium chloride which contained the radioactive element to an extent sufficient to show an "activity" 900 times greater than that of uranium, gave values practically the same as those of ordinary barium, namely 137.4. That is to say, the actual amount of radium which gave rise to so high an "activity" in the barium chloride was too small to influence the atomic weight determination. When, however, the concentration of the radium chloride in the barium chloride was considerably increased by a continuation of the fractionating process, the atomic weight of the metal was found gradually to rise. Thus, when the intensity of the radioactivity reached 3000 times that of uranium, the atomic weight of the "barium" rose to 140; while with a concentration representing a radioactivity 7500 times that of uranium, the atomic weight of the metal present was found to be 145.8. From these determinations it was evident that radium would be found to be an element of very high atomic weight, and in the course of time when it became possible to obtain small quantities of radium compounds—such as the chloride and bromide—in a state of comparative purity, this was found to be the case. The latest determinations (Curie, *Compt. rend.* 1902, 135, p. 161) have assigned the number 225 as the atomic weight of this new element—a value which the discoverers regard as being correct to one unit. From purely spectroscopic considerations, however, Runge and Precht (*Ast. Journ.*, April 1903) calculate the atomic weight of radium to be 258.

The element radium appears to resemble barium in its chemical relations. Thus the sulphate is insoluble in water and in acids; the carbonate is insoluble in water, and the chloride is precipitated by both strong hydrochloric acid and alcohol.

As seen in the Bunsen flame, the strongest and most permanent line produced by radium bromide is the blue line 4826.

The metal itself has not yet been isolated,* and in view of the extreme

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* In the literature of the subject the name ***radium*** is constantly employed when in reality a ***radium salt*** is intended.

minuteness of the quantities of this element which occur in the mineral pitchblende this need be no cause for surprise. Not only is the amount of radium present in this mineral too small to be detected by any chemical test, but the spectroscope itself does not afford a sufficiently delicate means for its detection; and it is not until the quantity naturally present has been greatly concentrated by the process already described, that the characteristic spectrum even begins to make its appearance.

The chief interest attaching to this new element is associated with the strange property it possesses in such a high degree of emitting "radiations." Radium bromide, for example, is self-luminous in the dark; the rays it emits are capable of acting upon a photographic plate, much as the Röntgen rays affect it. They cause phosphorescence upon a screen of barium platinocyanide, and produce radiographic effects similar to those given by the "X" rays. They are capable of penetrating metals, and will discharge an electroscope not only through considerable intervals of space, but also through screens of various materials.

Most mysterious of all, they appear to possess the power of exciting a temporary radioactivity in other substances otherwise inactive. Thus, if a solution of a radium salt and some distilled water are placed in separate dishes in a perfectly closed space, radioactivity is communicated to the water. The water, however, gradually loses this power even in a closed space, while it rapidly loses it if exposed. It has been found also that the intensity of this "induced" radioactivity is the same for all substances, under the same conditions, irrespective of their chemical nature.

Concerning the nature and the cause of the radiations emitted by radium and the other two well-defined radioactive elements uranium and thorium,* a large amount of experimental work has been done, and much speculation put forward. As the outcome of the former it has been established that at least four distinct, and to some extent separable emissions, may go to make up what is included in the term "radiations." These are distinguished as α, β, and γ rays, and "radioactive emanation."

1. *The α Rays.*—These rays are very easily absorbed by thin layers of matter. Thus, a thickness of aluminium 0.0005 cm. reduces their intensity to one-half. To them is mainly attributable the property of causing the ionisation of a gas, whereby its electrical conductivity is increased. They are deviated by a very strong magnetic field, the deviation being in the opposite direction to that exhibited by "cathode" rays. These α rays are not *waves* like ordinary light rays, but consist of actual matter, which is being projected at an enormous velocity, and is highly charged with positive electricity. They are described as a "flight of material particles," having a mass of the same order as the atoms of hydrogen,† and travelling with a velocity about one-tenth that of light.‡ These particles carry with them a relatively enor-

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* *Polonium*, and the still more recent *actinium*, are at present too undefined to be included as elements.

† *i.e.*, the ratio of the *charge* of the carrier to its *mass* is $\frac{e}{m}=6\times10^3$.

‡ That is, about 2.5×10^9 cms. per sec. (Rutherford and Soddy, *Phil. Mag.*, Feb. 1903).

mous amount of energy, each particle apparently having sufficient energy associated with it to excite phosphorescence visible to the eye. Thus, Crookes has shown that when a fragment of solid radium nitrate is brought near to a screen of "Sidot's hexagonal blende" (zinc sulphide), and the phosphorescent surface of the screen is examined with a pocket lens, it is seen to be dotted all over with brilliant specks of green light. In proportion as the radium salt is brought closer to the screen, these flashes or scintillations become more brilliant and more numerous, following each other with such rapidity that the surface presents the appearance of a "turbulent luminous sea."

"It seems probable that we are here *actually witnessing* the bombardment of the screen by the electrons hurled off by the radium" (Crookes).

2. *The β Rays.*—These rays are readily deviated by the magnetic field; and also differ from the α rays in their greater penetrating powers. Thus, while the intensity of the latter is reduced to one-half by passing through 0.0005 cm. of aluminium, the β rays are able to traverse a thickness of 0.05 cm. of this metal before their intensity is halved. A sheet of mica 0.01 cm. thick will completely absorb all the α rays, while it transmits the β and also the γ rays without appreciable diminution. The β rays, like the α rays, also consist of projected particles with a high velocity, but in this case they carry a *negative* electric charge, and their mass is believed to be greatly less than that of the particles constituting the α rays, namely, about the $\frac{1}{1000}$ of that of the hydrogen atom (Rutherford and Soddy, *Phil. Mag.*, May 1903). β rays are similar in all respects to the "cathode" rays emitted from a vacuum tube, except that the velocity of the particles is greater and consequently they are more penetrative. Their velocity is estimated to be between 2×10^{10} and 3×10^{10}.

3. *The γ Rays.*—These are non-deviable by the magnetic field, and closely resemble the Röntgen or "X" rays. They are far more penetrating than either the α or β rays, being capable of penetrating a thickness of 8.0 cms. of aluminium before their intensity is reduced to one-half. These rays are believed to be a *wave motion*, and not to consist of projected particles of matter.

4. "*Radioactive Emanation.*"—The elements thorium and radium * possess the property of emitting something which has the power of imparting radioactivity to any substance in their immediate neighbourhood. The radioactivity thus imparted or excited is only of a temporary character, its intensity diminishing and dying away when the substance is removed from the influence of the original radioactive body. Experiments seem to prove that these effects are not produced by any of the rays already described, but are due to some other distinct emission, and the term "radioactive emanation," or shortly "emanation," has been adopted to denote this.

The radioactivity which is thus imparted to substances in the proximity of these radioactive elements (usually spoken of as excited radioactivity) is believed to be caused by the deposition upon their surface of radioactive matter, which is transmitted by positively charged carriers; while the radio-

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* Uranium appears not to share this property.

activity of the "emanation" itself is believed to be due to the emission from it of α rays only. When a small quantity of thorium oxide* is placed in a tube (the oxide being enveloped in material capable of intercepting the ordinary radiations) and a stream of air is passed over it, the air is found to carry with it the "emanation" which the thorium oxide gives out; and the issuing stream of air, even after being conveyed through many feet of tube, is capable of discharging an electroscope. In the case of radium compounds the amount of this "emanation" was found to be comparatively small when the radium compound is employed in the solid state, but when the radium salt is dissolved in water, the "emanation" appears to be given off in a sudden rush, as it were, and the solution continues to emit this "emanation" in amount many hundred times as great as was produced by the solid salt. A similar enormous increase also takes place when the radium compound is heated. These observations have led to the belief that the "emanation" is actually occluded by the solid compound.†

In many other respects this "emanation" behaves like an inert gas. Thus if the stream of air carrying the "emanation" is passed through a tube plugged with cotton wool, nothing is arrested or filtered out by the wool and the radioactivity of the air as it issues is not diminished. Neither is it affected by the air being bubbled through strong sulphuric acid, or passed through a red-hot platinum tube. When air conveying "emanation" is slowly passed through a U-tube cooled by liquid air, the "emanation" is completely condensed, and the air which passes out is entirely free from all trace of this substance. If a glass tube is employed, and the air current is sufficiently slow, the progress of the condensation can be traced by the fluorescent appearance of the glass, showing that the condensation has all taken place upon the first portions of the tube traversed by the stream of air. If now the tube is closed at both ends and the temperature allowed to rise above a certain point, the condensed "emanation" appears to vaporise again, and the fluorescence extends throughout the entire length of the tube. The volatilisation point of radium emanation appears to be about −150°, while that of the thorium emanation is given as about −120° (*Phil. Mag.*, 1903, p. 575).

In the case of thorium, the "emanation" loses its radioactivity, or *decays*, much more rapidly than the radium emanation. Thus, while the activity of thorium emanation falls to half its intensity in the space of one minute, the intensity of the radium emanation only sinks to half its value in the space of four days, while still retaining sufficient activity to be detected after the lapse of one month. This rate of decay of the radioactivity of the "emanation" is the same even at the low temperature of liquid air, and it is considered probable that the marked difference in the rates of decay of the "emanation" from thorium and radium may account for the difference observed in their vaporisation temperatures.

It was at one time supposed that the radioactivity of these radioactive elements was not a property intrinsic to the elements themselves, but was due

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* Most of the earlier work by Rutherford and Soddy (*Phil. Mag.*, 1902) in this connection was done with thorium compounds.

† Rutherford and Soddy, *Phil. Mag.*, 1903, p. 449.

to the presence in small and varying quantity of some unknown substance. Crookes found (*Proc. Royal Soc.*, 1900) that by processes of a purely chemical nature he was able to separate from uranium nitrate small quantities of material which seemed to possess all the radioactivity, leaving the bulk of the uranium compound inactive. He applied the name Uranium X to this "unknown uranium." Similarly in the case of thorium; when the hydroxide was precipitated by ammonia, and the filtrate (which chemically should contain no thorium) was evaporated to dryness and ignited to expel ammonia salts, minute residues were obtained which were many hundred times more active than an equal weight of thorium oxide (Rutherford and Soddy, *Phil. Mag.*, September 1902). The precipitated hydroxide, although not entirely robbed of radioactivity, was found to have its activity greatly reduced. This supposed "active" constituent was therefore called Th X. Later investigations, however, revealed the remarkable fact that the thorium compound which had thus been partially deprived of its radioactivity gradually *regained* it when left to itself; while the separated Th X gradually *lost* it. Moreover, it was found that the two processes went on exactly at the same rate, that the rate of decay of the activity of Th X was the same as the rate of recovery of activity of original thorium compound. From this it would appear that two opposing processes are simultaneously going forward in a radioactive substance, namely, the continual production of fresh radioactive material and the constant decay of the radiating power of the active material. In other words, what may be called the *normal* radioactivity is a condition of equilibrium, where the rate of increase of activity due to the production of fresh active material balances the rate of the decay of the activity in the radioactive material already formed.

The views now generally held are that the phenomena of radioactivity are due to atomic changes, but changes of a character altogether different from any that have previously been dealt with in chemistry. It is believed that the atoms of these radioactive elements (which, it will be noted, are possessed of the highest atomic weights of all the elements) are undergoing a process of disintegration or degradation: that in the course of their movements, owing to some combination of conditions about which at present we know nothing, the kinetic energy of some of the atoms reaches a point beyond which the stability of the atom is no longer possible. Under these circumstances the atom breaks up, throwing off some *matter* from itself, and assumes a more stable configuration. The particles or fragments of the original atoms themselves undergo further changes, giving off other particles, thus giving rise to the various phenomena of radioactivity.

In the case of radium there seems to be indubitable evidence (based on the work of Ramsay and others) that one of the final products of the radioactive change is the element *helium*. A minute quantity of radium emanation enclosed in a Plücker vacuum tube was found after the lapse of a few days to give the characteristic spectrum of helium.

It has been further suggested (Boltwood, *Phil. Mag.*, 1905) that radium itself is a product of the radioactivity of uranium; not necessarily a *first* product, but probably through one or more intermediate stages.

If these are the true interpretation of the phenomena of radioactivity we are undoubtedly face to face with an actual instance of the "transmutation of the elements," which has hitherto been regarded only as an idle dream of the alchemist. It may, indeed, be that in these radioactive processes we have as it were a peep into the unknown region of the "evolution of the elements."

The energy which is liberated during this process of atomic disintegration is enormous, taking into account the minute quantities of matter concerned. M. and Mme. Curie have shown that a sample of a radium salt gave out energy sufficient to melt half its own weight of ice per hour. This energy, which is stored up in the atoms of these elements, the "internal energy of the chemical atom," as it has been termed, and which is set free during radioactive change, is of an entirely different order of magnitude from that which is disengaged during any processes of ordinary chemical change. It has been calculated, indeed, that the energy of radioactive change is many thousand times, or even a million times, as great as that of any known chemical change, when equal weights of matter are concerned. The idea of an atom as a *system*, and, moreover, one capable of undergoing changes into simpler systems, is a view which, to the chemist, may at first seem strangely heterodox, and one altogether opposed to fundamental doctrines of chemistry. In reality, however, this new view as to the constitution of an atom does not touch the question of the indivisibility of the atom in the purely chemical sense. From this point of view the *chemical atom* still retains its position as the lowest stage in the complexity of matter, and may still be defined as the smallest particle of matter *which can take part in a chemical change.* The chemical atoms of these radioactive elements are not divisible into what may be called "chemical fragments." If the atom is a *system*, then in all *chemical* reactions and changes the system in its entirety takes part. When it is borne in mind that the weight of matter which the atom, regarded as a changing system, throws off in the form of "radiations," "emanation," or "electrons" is so infinitely minute, that it has been estimated that it would require many hundreds, if not thousands of years before enough of it could be collected to be detected by the most delicate balance, it will be evident that we are dealing with phenomena of a totally different order from those in which the relative weights of matter entering into chemical combination are concerned.