REVIEWS.

AN EXPERIMENTAL STUDY OF RADIO-ACTIVE SUBSTANCES.[1]

Professor Röntgen's remarkable discovery, in 1895, of the penetrating rays called by him X-rays, but now equally well known by his own name, was followed in 1896 by Becquerel's announcement that the salts of uranium emit invisible radiations capable of discharging electrified bodies and of producing skiagraphic images on sensitive plates. He found that potassio-uranic sulphate emits rays that pass through black paper and affect photographic plates; this property is not limited to the brilliantly fluorescent uranic salts, but is shared by the non-fluorescent uranous salts. All uranium compounds examined proved to be active, whether phosphorescent or not, whether crystalline, melted or in solution; and metallic uranium exhibits the phenomena in a marked degree. The permanence of this property is amazing, substances kept in a double leaden box more than three years emitted rays having almost as much power as when first tested.

Shortly after the announcement by Becquerel, experimenters found that other substances have the power of emitting these "Becquerel rays;" M. Henry found it in phosphorescent zinc sulphide, Niewenglowski in insolated calcium sulphide, Troost in artificial hexagonal blende, and Schmidt in thorium compounds. In 1898 Mme. Sklodowska Curie, working in the laboratory of the Municipal School of Industrial Physics and Chemistry in Paris, devised a special apparatus for measuring the electrical conductivity of the air when under the influence of "radio-active bodies," and by its means studied the behavior of the minerals pitchblende, chalcolite, autunite, cleveite, monazite, orangeite, and thorite, and found them all active. Some varieties of pitchblende showed more than three times as much energy as metallic uranium itself, and this led her to the conclusion that the peculiar property was due to some unknown body contained in the mineral, and not to uranium compounds. Associating with her, her husband, Mme. and M. Curie attacked the mineral pitchblende with acids and reagents and soon obtained results that were presented by M. Becquerel to the Academy of Sciences, Paris, at a meeting held Monday, 18th July, 1898.

These savants showed that pitchblende contains a substance, apparently analogous to bismuth, which emits Becquerel rays

[1] Read at a meeting of the Chemical Society of Washington, held April 21, 1900, at Baltimore, Md.

4000 times stronger than uranium; they were unable to isolate the element having radiant power but they named it "Polonium," in honor of the native land of Mme. Curie. In December of the same year the lady received the Gegner prize of 4000 francs awarded her by the Academy of Sciences, and later in the same month M. and Mme. Curie, together with M. Bémont (director of the Municipal Laboratory), announced the discovery of a second radio-active body in pitchblende, which they called "Radium." Since that date Mme. Curie and her husband have industriously carried on investigations, publishing their results in the *Comptes rendus*; and some German physicists, not gallant enough to leave the enterprising woman a clear field, have announced some minor discoveries. From these papers we gather the following facts concerning these marvelous bodies.

As yet, comparatively little is known of the chemistry of the salts of polonium, since the radio-active substance has not been separated from its companions; on working up the mineral pitchblende the polonium is found in the precipitate thrown down by hydrogen sulphide, and insoluble in ammonium sulphide. Solutions of polonium react like those of bismuth, being precipitated by water.

The mixture of substances in which radium shows its activity has been more fully studied; the yet unknown element accompanies barium in analytical separations, its chloride is wholly soluble in water, and it responds to the usual tests for barium. The spectrum of the substance shows the bands of barium together with other lines peculiar to radium.[1] Attempts to separate radium from barium have been unsuccessful, but by fractional precipitation of the mixed chlorides with alcohol a salt has been obtained having 900 times the activity of uranium.

By operating on half a ton of the residues of uranium minerals, Mme. Curie obtained 2 kilograms of material rich in radium; with this, attempts were made to determine the atomic weight of radium, and she found the figures 140, the atomic weight of barium being 136.4.

The extraordinary physical properties of the rays emitted by these bodies have commanded the most attention; they possess luminosity, actinic and skiagraphic power, and render the air through which they pass a conductor of electricity. This latter property, the one which led to their discovery, is studied by means of an electroscope of special construction. It consists essentially of a gold-leaf (or aluminium foil) electroscope enclosed in a metallic box with glass sides and communicating with a metal disk exterior to the box. This disk lies in a horizontal plane a few centimeters above another parallel disk which serves as a support for the substances under examination.

[1] Demarcay: *Compt. rend.*, 129, 716, Nov. 6, 1899.

When the electroscope is charged by rubbing the upper disk with a piece of ebonite, the gold-leaf diverges from the perpendicular and will remain so for some time if undisturbed; on placing a layer of any radio-active body on the insulated lower disk the air between the two disks becomes a conductor and the gold-leaf at once resumes its normal position. To estimate the rapidity of the displacement of the gold-leaf, a microscope fitted with a micrometer eye-piece is attached to the apparatus at right angles to the axis, and with the aid of a watch beating seconds the time is noted which the gold-leaf takes to reach a certain point on the scale of the micrometer.

Becquerel first announced that the rays given out by uranium exhibited the phenomena of polarization, reflection, and refraction, but this was not confirmed by other observers and on repeating his experiments with radium and with polonium Becquerel got contradictory and negative results. The French chemist observed that the rays emitted by different bodies are very unequally absorbed; the rays of radium and uranium freely penetrate plates of quartz, fluorite, and mica, but those of polonium are absorbed by these minerals and scarcely penetrate paper. On the other hand rays of polonium pass through aluminum more freely than those of uranium.

The rays of divers origin are also influenced in different ways by a magnetic field; in an irregular magnetic field formed by a powerful electromagnet, the rays emitted by radium are deflected and concentrated on the poles; to show this, Becquerel devised ingenious experiments giving photographic records.[1] On examining the rays of polonium compounds (furnished by Mme. Curie) he found that polonium acted differently from radium,[2] and his results failed to confirm the observations of Geisel previously announced. Later, Mme. Curie also published a note on the dissimilar behavior of the rays of polonium and of radium in a magnetic field.[3] The subject has also been studied at Vienna by Stefan Meyer and Egon R. von Schweidler.[4]

Becquerel rays excite phosphorescence in gems, minerals, barium sulphide, calcium sulphide, etc.; in fluorite the phosphorescence remains twenty-four hours after the influence of radium has been removed, much as when exposed to the light of the electric arc.

In studying the power that these rays have of communicating energy to inactive bodies, Mme. Curie worked with substances so well purified that they were 50,000 times more powerful than uranium, and the induced activity measured 1 to 50 times that

1 *Compt. rend.*, **130**, 996, Dec. 11, 1899.
2 *Ibid.*, Dec. 26, 1899.
3 *Ibid.*, **130**, 73, Jan. 8, 1900.
4 *Phys. Ztschr.*, **10**, 113.

of uranium; the substances examined were zinc, aluminum, brass-foil, lead, platinum, bismuth, nickel, paper, barium carbonate, and bismuth sulphide. Her experiments showed that a true induction of radiant energy is effected, and the energy imparted to metallic plates is not removed by washing with water although the radium chloride ("chlorure de barium radifère") is soluble. The activity induced by Becquerel rays persists, while that caused by Röntgen rays ceases suddenly on removal of the agent.

The actinic power of the rays is shown by exposing the salts to sensitive plates; with the relatively pure material obtained by Mme. Curie an exposure of one-half minute sufficed to get an impression. The peculiar power of Röntgen rays is seen by using a barium platinocyanide fluoroscope, the rays exciting fluorescence through aluminum, vulcanite, etc.[2]

Mme. Curie records obtaining good "photo-impressions" with uranium, uranous oxide, pitchblende, chalcolite, etc., through glass, air, and aluminum.

The spontaneous luminosity of radium compounds was announced by Mme. Curie to the Physical Society of Paris in March, 1899,[3] and in November of that year she published her discovery that the wonderful rays exert chemical action. They transform oxygen into ozone; this was first noticed by the odor of the air in a flask in which radium compounds were confined, and was confirmed by the usual test with potassium iodide starch-paper. The rays also produce a certain coloration in glass changing it to violet; and they transform barium platinocyanide from yellow to brown, in which state it is less fluorescent, but this can be revived by insolation.[4]

At the suggestion of Mme. and M. Curie, M. A. Debierne, working in the laboratory of the Sorbonne, examined pitchblende for other radio-active bodies, especially the portion precipitated from solution by ammonia and ammonium sulphide, after separation of the uranium; in October, 1899, he found associated with titanium, a substance exhibiting 100,000 times more radiant power than uranium, and having chemical properties distinct from radium and polonium. The rays emitted by this body, named actinium, have the same manifold action as the other substances, with the exception that it is not self-luminous.[5]

In a more recent paper[6] M. Debierne finds that actinium is

1 *Compt. rend.*, **124**, 714, Nov. 6, 1899.
2 *Ibid.*, **126**, 1101 (1898); **127**, 1215, Dec. 26, 1898.
3 *Rev. chim. pure et appliquée*, July, 1899.
4 *Compt. rend.*, **129**, 823 (Nov. 30, 1899).
5 *Ibid.*, **129**, 593.
6 *Ibid.*, **130** (April 12, 1900).

allied to thorium, and suggests that the radio-activity of the latter is due to admixture of the new substance.

To complete this review of the radio-active bodies, brief notice must be made of two papers by German chemists. Fritz Geisel obtained radium from uranium ores other than pitchblende, and remarks: "Freshly crystallized Ba salts containing Ra are only slightly active, but in a few days or weeks they reach a maximum. They are strongest when anhydrous, moisture stops activity and heating restores it."[1]

Becquerel rays have the same intensity in partial vacuum as at ordinary air-pressure; this was proved by electrical and photographic experiments made by J. Elster and H. Geitel.[2]

Through the enterprise and liberality of the Smithsonian Institution, and by the courtesy of Secretary Langley, I have enjoyed the opportunity of studying small specimens of these rare and costly substances; they comprise 10 grams of "radio-active substances" in two portions, prepared by E. de Haen, manufacturing chemist of Hannover, Germany, and 4 grams of "chlorure de barium radifère," and 4 grams of "polonium subnitrate" from the "Société Centrale de Produits Chimiques (Ancienne Maison Rousseau)", Paris, said to be prepared according to the instructions of Mme. and M. Curie.

The samples from Hannover were marked "A" and "B" respectively, and a memorandum accompanying them stated that "B" excites fluorescence in barium platinocyanide more energetically than "A," whereas the latter is self-luminous; as a matter of fact I found both luminous in the dark and "B" the brighter of the two.

The specimens were enclosed in hermetically sealed bottles and protected from light by straw-board cylinders; on removing the wrappings in a dark room both were seen to emit greenish white light that gave to the enveloping papers a peculiar glow, similar to the fluorescence produced by Röntgen rays. I here call especial attention to the fact that during all the time that I have had the substances under examination they have been kept in the dark, no light reaching them stronger than that of the yellow and orange-red of a photographic dark room, so that insolation has played no part in renewing their energy.

The grayish white powders proved to be wholly soluble in water and the solution gave the usual reactions for barium chloride.

Moistening the radium chloride with cold water does not immediately stop emission of light, but on heating to boiling, the luminosity ceases. The water was expelled and the material, heated in a platinum dish to dull redness, resumed its luminosity

1 *Ann. Phys. Chem.*, 69, 91 (1898).

2 Wied. *Ann.*, 66, 135 (1898).

after a few days *in the dark*. The fact that radium compounds resume their power of emitting light slowly has been noted by Geisel, but he fails to state whether the salt regains its property without exposure to sunlight.

The substances "A" and "B" were examined with a fluoroscope at first without success, but in a perfectly dark room, after the eyes became sensitive, the screen of barium platinocyanide was distinctly seen to fluoresce feebly.

The small specimens of these bodies had no perceptible influence in exciting phosphorescence of sulphides of the alkaline earths exposed to their action.

Having at hand no apparatus for measuring the electrical conductivity of the air, my experiments were chiefly directed to ascertaining the action of the rays on sensitive plates.

The photographic experiments were made with Seed non-halation dry plates (No. 26). To test the approximate actinic power of the bodies "A" and "B," sections of sensitive plates at distances of 5 and 10 inches were exposed at intervals of from two to twelve minutes; these gave bands varying in intensity with the duration of action. "B" showed far greater power than "A". By exposing sensitive plates behind an ordinary negative to the entire 10 grams of "radium" from two to three hours, good transparencies were obtained; on substituting Eastman's bromide paper, prints were secured; the distance of the sensitive surfaces from the source of light was about 3 inches.

To get skiagraphic images, plates were enveloped in Carbutt's black paper (non-permeable to light) and on this was laid a piece of tin-foil cut in open work pattern; after one hour's exposure a negative was obtained plainly showing the pattern. "A" was apparently stronger than "B".

Analogous experiments were carried out with the specimens of "radium" and of "polonium" from Paris; making allowance for the difference in weight, the radium of German origin was about five times as active as the French. The sample labeled "polonium subnitrate" (weighing 4 grams), had positively no action on the plates used.

Having at my disposal 500 grams exceedingly well purified uranic nitrate (remaining from previous researches), I examined it for Becquerel rays, but a sensitive plate exposed three hours to the beautifully fluorescent crystallized salt gave no trace of action. Similar negative results have been obtained by Sir William Crookes.

The primary source of the energy manifested by these extraordinary substances has greatly puzzled physicists and as yet remains a mystery. Mme. Curie speculating on the matter, at first proposed the following explanation: she conjectured that all space is continually traversed by rays analogous to Röntgen rays but far more penetrative, and not capable of being absorbed by certain elements of high atomic weight such as uranium and thorium.

Becquerel, reflecting on the marvelous spontaneous emission of light, remarked: if it can be proved that the luminosity causes no loss of energy, the state of the uranium is like that of a magnet which has been produced by an expenditure of energy and retains it indefinitely, maintaining around it a field in which transformation of energy can be effected. But the photographic reductions and the excitation of phosphorescence in a sensitive screen require an expenditure of energy, of which the source can only be in the radio-active substances. As this expenditure is slight perhaps the bodies have a large reserve of energy which can be drawn upon for years without showing loss; at any rate it has been impossible, says Becquerel, to bring about any appreciable variation in the intensity of the emission by physical influences.

Somewhat later Becquerel hazarded the opinion that the radiation of radium is composed at least in part of cathodic rays; but these have been proved to be material, hence the induced activity must be caused by material particles impinging upon the substances excited. This materialistic theory seems to be confirmed by the results of ingenious experiments made by Mme. and M. Curie; they placed a sensitive plate beneath a salt of radium supported upon a slab of lead, in the vicinity of an electromagnet. Under these conditions when the current was passing, the rays emitted by the chemical salt were bent in curved lines upon the sensitive plate, making impressions.

It may be objected, says a French writer in the *Revue générale des Sciences* that this theory requires us to admit actual loss of particles of matter, nevertheless the charges are so feeble that the most intense radiation yet observed would require millions of years for the removal of 1 milligram of substance.

The same writer raises the question, which of the observed phenomena is the primary one? does the radiation of radium excite cathodic rays, or do the latter exist in the chemical compounds? and he regards the latter as improbable. The primordial source of energy in radium probably resides, he adds, in the ultraviolet light, and the efflux of material particles that ensues is only a secondary phenomenon, but on a far larger scale than has previously been observed.

Speculations as to the future history and applications of these wonder-working bodies press upon even the dullest imagination; if a few grams of earth-born material, containing probably only a small percentage of the active body, emit light enough to affect the human eye and a photographic plate, as well as rays that penetrate with X-ray power, what degree of luminosity, of actinism, and of Röntgenism, is to be expected from an hundredweight of the quintessence of energy purified from interfering matter?

And to what uses is this light-generating material to be applied? Are our bicycles to be lighted with disks of radium in tiny lanterns? Are these substances to become the cheapest form of light for certain purposes? Are we about to realize the chimerical dream of the alchemists,—lamps giving light perpetually without consumption of oil?

Seriously, in what direction is profound study of these substances going to lead us? Will it not greatly extend our knowledge of physical manifestations of energy and their correlation? What bearing will this power of "opening up paths through the air" for currents of electricity have upon our knowledge of heat, light, electricity, and those forms of energy called by the names of Röntgen and Becquerel?

In what corner of the globe will be found the cheap and convenient supply of raw material yielding the radio-active bodies? Will not cnemists be obliged to reexamine much known material by laboratory methods conducted in the dark? Many of us have worked up kilograms of pitchblende to extract uranium oxides and in so doing have poured down the waste-pipe or thrown into the dust-bin the more interesting and precious radio-active bodies.

At all events whatever the future may bring, physicists are deeply indebted to Becquerel, and to Mme. and M. Curie for placing in our hands new methods of research and for furnishing a novel basis for speculations destined to yield abundant fruits.

POSTSCRIPT.

Bela von Lengyel, of Budapest, has pointed out that the chemical evidence is insufficient to establish the elementary character of these radio-active bodies, and claims to have prepared the so-called "radium" synthetically. By fusing with the heat of the electric arc uranic nitrate mixed with 2 to 3 per cent. of barium nitrate, and treating the mass with nitric acid, water, and sulphuric acid, successively, he obtained radio-active barium sulphate possessing all the physical properties characteristic of the "element" announced by Mme. Curie. The resulting substance gives out actinic rays, Röntgen rays, excites platinocyanide screens, and causes air to conduct electricity.

The Hungarian chemist has made and examined the chloride and the carbonate of this substance and finds that they have the same properties; he wishes his paper regarded as a preliminary notice, proposing to continue his researches.

Von Lengyel's paper was received by the German Chemical Society on April 2nd, but the number of the *Berichte*[1] containing it only reached Washington on May 26.

Admitting that radio-active bodies can be manufactured to order, are we any nearer explaining their mysterious powers?

HENRY CARRINGTON BOLTON.

COSMOS CLUB, WASHINGTON, D. C., May 26, 1900.

MODERN RESEARCHES ON THE CHEMISTRY OF THE PROTEID MOLECULE.[2]

It is impossible, at the present stage of our knowledge, to give any satisfactory definition of a proteid, based either on its physiological or chemical properties. Physiologically, it can be pointed out as the main constituent of all cells and tissues. In regard to its chemical properties, it can be stated with absolute certainty that it consists of carbon, hydrogen, oxygen, nitrogen, and sulphur. It does not possess very marked acid or basic properties, but forms salts with both bases and acids, its affinity for both being very weak.

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It can not be classified under any of the well-established groups of chemical compounds. Some attempts in this direction, however, have been made in recent years; and of these, the attempt to classify all proteids among glucosides has been the cause of much dispute from the experimental and speculative side of the question. The author of this theory and its most enthusiastic advocate was Pavy, who, by hydrolysis of egg albumin, succeeded in obtaining a reducing substance, capable of combining with phenylhydrazine, forming an osozone of a definite melting-point.

Physiologists, who were all inclined to see the source of the tissue-carbohydrates in the tissue-proteids, naturally welcomed Pavy's work, and were ready to endorse his views. A number of researches, however, were undertaken in order to test the correctness of Pavy's statements. The results thereof were contradictory. Morner has investigated, in that direction, serum globulin, and found that on heating with 3–5 per cent. hydrochloric acid, it yielded a solution capable of reducing Fehling's solution. Krawkow has tested, in the same direction, various proteids with different results. Substances combining with phenylhydrazine, giving osozone, were obtained by him from

[1] Vol. 33, p. 1237, May 14, 1900.

[2] Read before the New York Section of the American Chemical Society, May 11, 1900.