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CHEMICAL SECTION.

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Radio-Activity.

BY EDWARD A. PARTRIDGE and ROBERT H. BRADBURY.

I. HISTORICAL.

The history of science presents us with frequent illustrations of the fact that an erroneous hypothesis may be extremely helpful to the progress of knowledge. If an hypothesis is incorrect, investigation will reveal the error and the facts which are gathered in the course of the work will remain as a permanent heritage.

Radio-activity is a case in point. The investigations in this direction started from the idea that the Röntgen rays were due to the phosphorescence of the inner walls of the vacuum tube. It occurred to Becquerel that if this were true, then all phosphorescent substances should produce Röntgen rays when excited by light. To test this he wrapped a photographic plate in black paper, laid upon it a crystal of uranyl potassium sulphate—a highly phosphorescent substance—and exposed the whole to sunlight. The

plate was acted upon as he expected, but additional experiments revealed the surprising fact that an excitation of the uranium salt was unnecessary—the whole process occurred equally well in the dark. Further, it was found that uranium itself—which is not phosphorescent—exerted a more vigorous action on the plate than potassium uranyl sulphate.

At once it became necessary to drop the idea of rays excited by the action of light upon phosphorescent substances and to substitute the conception of uranium itself as a source of inexplicable radiations. All uranium compounds were found to be active, and there appeared to be a direct relation between the degree of activity and the uranium content.

At this stage (1898) P. and S. Curie began their remarkable work on the subject with a quantitative investigation of the radio-activity of a vast number of substances. Obviously the photographic method is unsuitable for quantitative work and can only give, at the best, rough approximations. Fortunately there is another effect of the Becquerel rays which can readily be measured—they confer upon air the power to conduct the electric current. If, then, two condenser plates are brought to a constant difference of potential and a radio-active substance is brought between them, a current will pass which can be measured. Other things being equal, the strength of this current will be proportional to the radio-activity of the substance. For rough work a charged electroscope is sufficient. The approach of a radio-active substance discharges it, and if the leaves are always brought to the same angle of divergence and the radio-active preparation held at the same distance, the time of discharge is an inverse measure of radio-activity.

Two of the results of this work of the Curies are especially important. First, compounds and minerals containing uranium and thorium are radio-active—in the absence of one of these elements radio-activity is not noticed. Second, some minerals containing uranium are far more active than uranium itself. Thus, chalcocite is about twice as active and some samples of pitchblende four times as active as metallic uranium.

Clearly it could no longer be held that the production of Becquerel rays is a property of the uranium atom, for in that case uranium would be the most active of all substances. Thus emerged the idea of elements of great radio-active energy accompanying uranium in its compounds. Varying radio-activity is easily accounted for by the supposition of a larger or smaller content of the real radio-active element. Guided by this thought, the Curies worked up large quantities of pitchblende by the ordinary analytical process, carefully testing each precipitate for radio-activity. The difficulty of the task was great, for pitchblende has an exceedingly complex composition, containing nearly all the known elements. The quantity of real radio-active substance in it is very small, probably one part in a million, so that it is necessary to work it up by the ton.

They were encouraged at the start by the observation that when the mineral is heated the sublimate obtained is much more active than the pitchblende itself.

II. PREPARATION AND PROPERTIES OF POLONIUM AND RADIUM.

In the course of this work the Curies found that the *bismuth* separated from the pitchblende was about 100 times as active as uranium. This led them to assume the presence in it of small quantities of a new radio-active element to which they gave the name of *polonium*. By various methods they were able to fractionate the precipitate and to increase its strength. But in all cases the radio-activity of the Curies' polonium preparations rapidly diminished with time and finally disappeared almost completely. This points to the conclusion that the Curies' polonium is simply bismuth which has been made secondarily radio-active by contact with the *radium* of the pitchblende.

Marckwald* has separated from the bismuth of pitchblende a radio-active substance which behaves in a very different way. He dissolved the active bismuth precipitate and subjected it to fractional electrolysis. The small quan-

* Berichte der deutschen chem. Gesellschaft, 35, p. 2285 ; 35, p. 4239.

tity of black substance first precipitated was intensely active. It appeared therefore that the radio-active element was a "nobler" metal—*i. e.*, had a smaller solution pressure—than bismuth itself. This led him to try the effect of placing a rod of bismuth in the solution. This was covered with a black coating and acquired an activity equal to that of the best radium preparations. The rays differ from those of radium in their complete lack of penetrating power. Wrapping the rod in filter-paper is sufficient to stop the radiation completely. This explains the fact that an increase in the thickness of the coating does not increase the strength of the radiation. The coating on one of Marckwald's rods weighed, when scraped off, only 5 milligrams. When it was heated a small quantity vaporized and the rest melted to a silvery globule which was extremely brittle. Since in the absence of concentration-differences in the solution a metal cannot precipitate itself, the new substance cannot be bismuth. Of late Marckwald has concluded that it exhibits the closest chemical similarity with tellurium, and proposes for it the provisional name *radio-active tellurium*. It is important to notice that the radiation of Marckwald's substance does not decrease with lapse of time. Bismuth rods coated in the way indicated are to be brought into commerce. They can be used for the purpose of distinguishing genuine diamonds, which phosphoresce on their approach, while imitation gems do not.

Let us now return to the work of the Curies. In the systematic separation of pitchblende they made the important observation that the *barium* obtained was strongly radio-active. The name *radium* has been given to the active element associated with the barium. In order to separate the two, various methods of fractionation must be resorted to. Thus radium chloride is less soluble in water and in very dilute hydrochloric acid. Giesel* finds that it is better to work with the bromides, since the solubility differences are greater. Radium has a higher atomic weight than barium, and Madame Curie followed the course of the

* Radio-active Substanzen und deren Strahlen. Ahrens' collection, vol. 7, p. 1. This article has furnished many facts for the present summary.

fractionation by determining the atomic weight, which steadily increased with the intensity of the radiation. In the following table the radio-activity is measured in terms of that of uranium as unity.

Radio-activity.	Atomic Weight.
60	138
3000	140
4700	140.9
7500	145.9
very great	175

She has obtained an atomic weight of 225 on a still purer preparation.

Giesel* kept track of the fractionation by means of the flame-color of radium, which is pure carmine.

The existence of radium is to be regarded as well established. The spectrum has been carefully examined by Demarçay, Giesel and Runge. Madame Curie has obtained practically pure RaCl_2 and Giesel, has obtained RaBr_2 in pure condition.

Radium bromide when kept in the air gives off bromine and acquires an alkaline reaction which is due to the formation of radium hydroxide. This absorbs CO_2 and passes into the carbonate. RaBr_2 is soluble in water, and the solution soon becomes yellow from the liberation of bromine. The crystals appear to contain an occluded gas—at least a gas escapes with effervescence when they are dissolved. A slow and apparently unlimited escape of gas takes place from the solution. The presence of a halogen somewhat complicates matters, but with non-halogen compounds the phenomenon is as simple as it is astounding. *The gas which is continuously liberated is a mixture of hydrogen and oxygen in the relation 2 : 1 by volume.*† There occurs, therefore, a kind of continuous electrolysis of the solution, but without any current or other assignable source of energy. The change is not a chemical reaction between the radium compound and the water, for already a quantity of hydrogen has escaped from Bodländer's solution, which corresponds to 10

* Berichte, 35, p. 3608 (1902).

† Bodländer. *Chemische Zeitschrift*, 2, p. 396 (1903).

atoms for every atom of radium it contains, and there are no signs of an end of the evolution. This simultaneous and separate escape of hydrogen and oxygen from the bosom of the same liquid gives a severe shock to certain old, cherished and well-grounded views about the activity of elements in the nascent state. Platinum, which exhibits a pretty general catalytic acceleration of reactions in which gases are formed and escape, retards this one since it brings about the reunion of the separated hydrogen and oxygen. Radium carbonate—an insoluble salt—produces a similar decomposition of water in which it is suspended. It has been remarked that a solution of radium bromide rapidly becomes yellow from separated bromine. The gas which is evolved from the liquid is a mixture of detonating gas with an excess of hydrogen equivalent to the bromine which has passed from the ionic to the molecular condition. This gas is itself radio-active, excites sensitive substances to phosphorescence and blackens the glass pipettes in which it is collected.

Radium compounds are luminous in the dark. One preparation containing radium and barium chlorides gave a light so bright that it was possible to read by it. The phosphorescence of pure radium compounds is bluish and intense, but soon fades. On the other hand, the impure preparations containing much barium retain their luminosity unchanged for years. When a radium preparation is brought near the closed eye there is a sensation of light which is probably due to the phosphorescence of the interior of the eye under the influence of the rays.

CHEMICAL AND PHYSIOLOGICAL EFFECTS OF BECQUEREL RAYS.

In Berthelot's* experiments on this subject the radium preparation was inclosed in a single or double-sealed tube so as to exclude the possibility of chemical action between it and the substance whose behavior was being investigated. Iodine pentoxide separated into iodine and oxygen. Nitric acid was colored yellow probably by a change of a similar

* *Compt. Rend.*, 133, p. 659.

character to its decomposition by light. However, in other cases the effects of the rays differed from those of light. Thus a solution of sulphur in carbon disulphide, which separates insoluble sulphur under the influence of light, remained unchanged by radium rays. Oxalic acid and acetylene, both of which are affected by light, were not acted upon. White phosphorus passes into red phosphorus under the influence of Becquerel rays. Oxygen is converted into ozone. Glass is colored brown or violet. Berthelot—who used a lead glass—considers that the change is due to the separation of metallic lead in the glass. Compounds of potassium and sodium are colored bluish-green or violet, the action being similar to that of Röntgen rays on the same substances except that it penetrates into the interior in place of being confined to the surface. The color fades when the substance is placed in the light. Elster and Geitel and Giesel believe that the colors are due to the separation of a small quantity of metal which forms a solid solution in the salt, and Giesel has produced similar effects by treating the haloid salts with the vapor of potassium or sodium. Paper becomes brown and brittle under Becquerel radiation and celluloid loses its solidity.

Many of the chemical effects just mentioned are endothermic and require a continuous supply of energy in order to bring the change about.

Inflammations on the fingers are a frequent sequence of work with radium preparations. Giesel placed a celluloid capsule containing a small quantity of a radium preparation against the skin of the arm for two hours. The result was a gradual but vigorous inflammation, followed by blistering and loss of the epidermis. Healing followed, but the growth of hair has not been renewed. The green parts of plants lose their chlorophyll under Becquerel radiation and turn brown or yellow. Seeds lose the power of germination.

The principal physical properties of the emanations from radio-active bodies are the following:

They render insulators temporarily conducting. A charged electroscope surrounded by air or paraffin is discharged in their presence.

Some of the rays are deflected by a magnetic field while others are not.

Solids are more or less transparent to them.

Many substances, such as barium platino-cyanide, fluoresce under the influence of the rays.

Radio-active substances continuously emit light and heat.

Some of the invisible rays are reflected according to the law for light.

According to Rutherford,* radium emits three kinds of rays which he denominates α , β and γ .

(1) The α -rays are readily stopped by thin layers of matter, even by tissue-paper, and produce the greatest part of the ionization of gases observed in ordinary experiments. They consist of positively charged particles.

(2) The β -rays consist of negatively charged particles and are similar in all respects to cathode rays. α and β -rays are deviated by a magnetic field.

(3) The γ -rays are not deviated by a magnetic field and are capable of great penetration.

The difference in penetrating power of the three classes of rays is shown by the following table, which gives the thickness of aluminium that reduces the intensity to one-half its original value:

α -rays, .0005 centimeters.

β -rays, .05 “

γ -rays, 8. “

The amount of energy given off by radium compounds as α -rays is about 1,000 times as great as that radiated as β -rays.

It has been established that the residual activity of uranium and thorium freed from uranium- x and thorium- x consists entirely of α -rays. The radiation from uranium- x consists almost entirely of β -rays, while thorium- x sends out both α and β -rays. It appears, therefore, that the emission of α -rays is independent of the β -rays.

A thin-walled tube containing a radio-active substance

* *Phys. Zeit.*, 1903, p. 235

should show a diminution of weight in consequence of the continuous loss of changed particles. Heydweiller has shown that this is apparently the case. The loss of weight is, however, extremely small with the quantities he used, about '0005 gram in four weeks. Rutherford points out that this may be due to the influence of the radiation upon the surface of the glass tube.

Curie and Laborde* have quantitatively examined the heat emitted by radium. One gram of radium gives off heat the amount of which is of the order of 100 gram calories per hour. One gram-atom of radium gives off per hour an amount of heat comparable with the heat produced by the combustion of a gram atom of hydrogen.

The measurements were made with a thermo-electric couple of iron and constantan, one junction of which was surrounded by radio-active BaCl_2 and the other by pure BaCl_2 . The observations were confirmed by the Bunsen calorimeter.

Lodge† remarks that the development of heat is probably connected with the emission of the positively charged particles. He calculates that the emission of 1,000,000 charged atoms per second, with a velocity one-tenth that of light, would represent an amount of energy equal to 1,000 ergs per second, which would correspond to heat enough to melt 1 milligram of ice per hour. The loss of matter would amount to $\frac{1}{20}$ of a milligram in a century.

The position of radium in the periodic system is the subject of a recent paper by Runge and Precht.‡

As is well known, the spectra of related elements are definitely analogous. Runge and Precht found that the strongest lines of radium are exactly comparable to the strongest lines of barium and to the corresponding lines of magnesium, calcium and strontium. Moreover, the lines in these spectra occur in pairs, and the distances between the lines of the corresponding pairs are related to the atomic

* *Electrician*, 1903, p. 970.

† *Nature*, 1903, p. 511.

‡ Runge and Precht: *Astrophysical Jour.*, 1903, p. 233.

weights of the elements to which they belong. The law is as follows: In every group of chemically related elements the atomic weights are proportional to some power of the distance between the lines of corresponding pairs. Usually the exponent of the power is not a whole number. This law can be transformed thus: "If the logarithms of the atomic weights and distance between lines of pairs be taken as co-ordinates the corresponding points of a group of chemically related elements will lie on a straight line."

This law is illustrated by *Fig. 1*, which is from Runge and Precht's paper. We see from this figure that, among the alkali metals, potassium is the only one that falls below the straight line through the remaining points. It is interesting to note that the law shows a comparatively large de

FIG. 1.

viation for potassium, since its atomic weight should be greater than that of argon to fit into the periodic system.

Fig. 2 shows the application of the law to the alkaline earth metals. Extrapolation gives 258 for the atomic weight of radium as opposed to 225, the value determined by Madame Curie. This would naturally be anticipated, since any impurity would lower the atomic weight, and it is very difficult to separate radium from barium. F. Rinne has found that the bromides of the two elements are isomorphous, so that it is probable that they would crystallize together in an isomorphous mixture. The number 225 fits the periodic system better in that it fills the gap between bismuth and thorium in the correct column.

For the atomic weight 258, radium would be displaced two rows farther in the column *Mg*, *Ca*, *Sr*, *Ba*, and a number of new unoccupied places would arise. The point remarked by Rutherford may be cited in support of the higher atomic weight. The greater the mass of the atom the more complicated is its probable structure, and electrons would be thrown off with greater ease.

Source of Energy.—Concerning the source of energy emitted by radio-active substances, we are absolutely in the dark. All that can be done is to mention some of the many hypotheses that have been offered to explain the phenomena.

(1) That the energy is chemical in character and is given off in consequence of a continuous modification of the *Ra*

FIG. 2.

atom. The enormous amount given out renders this supposition highly improbable. Demarçay has advanced the argument, against this idea, that the spectrum of *Ra* shows no modification at the end of five months. Demarçay's notion does not seem valid, since to produce a spectrum energy is added in large amounts.

(2) That radio-active materials absorb energy of ether disturbances that do not noticeably affect ordinary substances.

(3) That atoms of *Ra* and similar substances act selectively upon the moving molecules of the surrounding gas after the manner of Maxwell's demons. (Crookes.)

(4) That radio-active substances absorb gravitational energy. To prove this some radium compound in a dish

was placed under one pan of a balance. That pan was apparently lighter than usual; the loss of weight gradually decreased. A second experimenter, however, observed that placing an empty dish under a balance pan causes apparent loss of weight, the necessary condition for the success of the experiment being that the dish must be touched with the fingers. Ascending currents of warm air completely account for the phenomenon. Repetition of the original experiment by Froch,* using great precautions, has shown that no loss of weight and hence no absorption of gravitational energy takes place.

Induced Radio-activity.—Substances that have been exposed to the emanations of radio-active bodies become themselves temporarily active. The law of the decrease of induced radio-activity has been carefully studied by Curie.† When a body made active by remaining in an enclosed space with

FIG. 3.

a radium compound is brought into free air it loses its power to emit rays according to an exponential law. It loses one-half its activity in half an hour.

Radium or a radium compound is placed in a tube of the form shown in *Fig. 3*. If after a time it is sealed off at *A* the portion *B* shows radio-activity, which decreases according to an exponential law, falling to one-half in four days. If *B* is opened and the enclosed air allowed to diffuse with the air of the room, the decrease of activity follows the rapid exponential law, that is, it falls to one-half in half an hour. If the tube was vacuum before sealing the rapid law was followed; this was also the case if air was admitted after sealing. The emanation apparently comes from the walls of the glass vessel, since immediately after removing the air the intensity is unaltered.

* *Phys. Zeit.*, 1903, 318.

† *Phys. Zeit.*, 1903, p. 314.

The algebraic form of the law which the fall of intensity follows is:

$$I = I_0 e^{-\frac{t}{\theta}}$$

I = intensity at time t .

I_0 = initial intensity.

t = time since first observation.

θ = a constant time = 5.752 days.

Some observations were continued for twenty days, I had then fallen to $\frac{1}{27}$ its initial value.

FIG. 4.

I falls to one-half its initial value in three days, twenty-three hours and forty-two minutes.

The constant θ remains the same under widely differing conditions. The following are some of the modifications of the experiment; in all cases θ was found to be the same:

- (1) Radium solutions of very different activities were used.
- (2) Solid Ra Cl_2 .
- (3) Form and dimensions of tube varied from 3 centimeters to 2,000 centimeters.
- (4) Thickness of glass walls changed.

- (5) Copper and aluminum vessels used in place of glass.
- (6) Induction took place through tubes long and capillary, or short and wide.
- (7) Time of induction varied between fifteen minutes and one month.
- (8) Pressures varied from 1 atmosphere to 2 centimeters of mercury.
- (9) Hydrogen or carbon dioxide used instead of air.

The same law is observed whether the external emanation or the internal conductivity of the tube is measured. Temperature has no influence upon the rate of loss of induced radio-activity. After some measurements were made with some tubes, they were maintained at a temperature of 450° for three days, then brought to normal temperature; the intensities of the radiations were the same as if they had been continually at the normal temperature. Other tubes were kept in liquid air for six days, at the end of which time they showed an activity abnormally low. After they had remained at the ordinary temperature for half an hour the intensity had risen to what it would have been if they had never been cooled. These facts are illustrated in *Fig. 4*, in which abscissæ are times in hours and ordinates are logarithms of intensities. Line 1 shows the decrease of intensity at ordinary temperature. Line 5 illustrates the experiments in which the tubes were heated to 450° , the dotted portion relating to the time during which the heating took place. Line 6 refers to investigation of the effect of refrigeration; the dotted line here shows time during which the tubes were cooled.

CENTRAL MANUAL TRAINING SCHOOL,
Philadelphia, April, 1903.

A GOOD ENGINE RECORD.

A straight line engine, in use at the works of the Solvay Process Company, in Syracuse, N. Y., recently completed a continuous run of 22 months, during which period it had not once been stopped. Its speed was 250 revolutions per minute, which makes 15,000 per hour, 360,000 per day, nearly 11,000,000 per month, and a grand total for the 22 months of some 241,000,000 revolutions without a stop. This speaks well for the excellence of the design and workmanship expended upon the engine, and for the excellence of the attendance received.—*Iron Age*.