

A FEW CHEMICAL CHANGES INFLUENCED BY RADIUM: A
NEW METHOD FOR THE DETECTION OF AMYGDALIN.*—
By H. JERMAIN M. CREIGHTON, M. A., Dalhousie
University, Halifax, N. S.

Read 13th April, 1908.

Up to the present time only a comparatively small amount of work has been carried out on the effect of radium on chemical reactions. Hardy and Wilcocks¹ have investigated the oxidation of iodoform, when acted on by Röntgen rays and by radium, and Hardy² has observed the coagulation of globulin under the influence of the latter. Becquerel³ found that white phosphorus is changed into the inactive red phosphorus, and that mercuric chloride in the presence of oxalic acid is reduced to mercurous chloride by the radiations from radium. The Curies⁴ have shown that the rays from radium change oxygen into ozone and discolour glass. Berthelot⁵ cites the following cases: iodic acid is decomposed by radium rays and by light, with liberation of iodine, the change being much slower than that of iodoform; nitric acid gives off nitrous fumes when acted upon by radium rays and by light. The decomposition of hydriodic acid has been observed and studied by Creighton.⁶ These, as far as I have been able to discover, are all the reactions that have been investigated up to the present time.

When it had been decided to investigate what influence radium had on different chemical changes, it seemed probable that the best results would be obtained if the radium were allowed to act on the substances that were to be transformed, under the conditions most favourable to the transformation. It was mainly for these conditions that the following substances were chosen.

*Contributions from the Science Laboratories of Dalhousie University [Chemistry.]

¹ Proc. Roy. Soc., 72, 480, 200.

² Proc. Phys. Soc., 1903, May 16.

³ C. R., 1901, 133, p. 709.

⁴ C. R., 1899, 129, p. 823.

⁵ C. R., 1901, 133, p. 659.

⁶ Proc. & Trans. N. S. Inst. Science, XII, 1, 1.

Five milligrammes of radium bromide of activity of about 1,000,000 were employed. The radium was enclosed in a small glass tube, so that only the α - and β -rays were used.

Action of Radium on Lead and Tin.

After a particularly cold winter, 1867-68, it was found that some blocks of tin that had been stored in the customs house at St. Petersburg, had mysteriously crumbled to a grey powder. It has since been shown that tin exists in two allotropic forms, one of which is this grey powder, the other the ordinary white malleable metal. The transition temperature of these two varieties of tin is about 20° C., the former being stable below, and the latter above this temperature. The reason all ordinary tin, most of which is at a temperature below that of transition, does not change into the grey kind, is due to its being in a state of unstable equilibrium, and kept there by an unknown agent, to which the name passive resistance has been given. If in some way this passive resistance could be overcome, then the transition of white into grey tin would readily take place.

It was in order to see whether radium would do this that the following experiment was carried out.

Two pieces of white tin, about two and a half centimetres square and a millimetre thick were prepared from pure mossy tin, and their surfaces made smooth and clean. These were placed in a small leaden box, Fig. 1, and separated from each other by means of a leaden partition, which was sufficiently thick to keep all but the fastest β -rays from passing from one compartment to the other. The ends of the box were left open. The

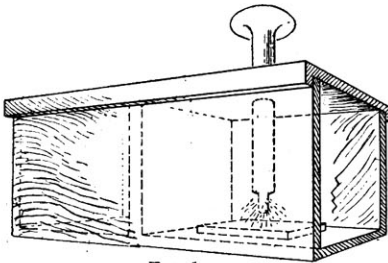


Fig 1

small glass tube, containing the radium, was held in the end of a hollow brass rod; this latter passed through a hole in one end of the leaden cover of the box, so that the radium was over, and about a millimetre distant from, the square of tin in one of the compartments of the box. This box was placed in a large tin box and kept at a temperature of about 0°C . for four months.

At the end of that time, the pieces of tin were taken out and examined under the microscope, and it was found that there was a formation of grey tin on the surface of each, but that the amount on the piece that had been bombarded by the rays from the radium, was greater than that on the piece which had not been so acted upon. This difference, however, was not very great, but the lead box which had contained the pieces of tin, had undergone a curious change, during the four months. The inside of the compartment into which the tube containing the radium had penetrated, was completely covered, with the exception of the bottom, with a thin white film, which was present in some places, particularly the top of the box, in relatively large quantities, while the other compartment did not contain the most minute trace of this substance. Around the hole in the top of the box, where the tube containing the radium entered, the lead was coated with the white substance, much more thickly than anywhere else. Some of this powder was scraped off and analysis showed that it was lead carbonate.

The only explanation the author can give of its formation is this. Some of the rays from the radium, after striking the surface of the tin, which was probably not perfectly even, were reflected upward, and bombarded the top of the lead box and ionized it, thus making it more active than it was. The portions of the lead which were thus made active, were able to combine with the moist carbon dioxide in the air, with the production of lead carbonate. This seemed to be borne out by the fact that it was the top of the box that was most coated with the carbonate.

The Action of Radium on Hydrogen Peroxide.

The action of radium on hydrogen peroxide was next investigated, as on account of its behaviour under the influence of light,¹ it was believed that it would be affected by radium rays.

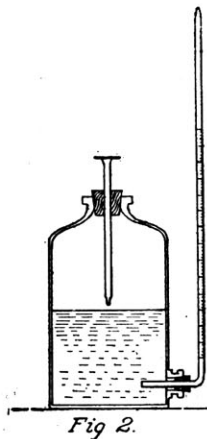
The hydrogen peroxide solution used in these experiments had a strength of 4.832 grams per litre.

Since hydrogen peroxide, when it decomposes, breaks up into water and oxygen, its decomposition can be estimated by measuring the oxygen produced, or the amount of hydrogen peroxide left in the solution by titrating with potassium permanganate. As this latter method necessitated changing the amount of substance in the system, the former was chosen, and the oxygen was measured by the change of pressure it produced.

A large reagent bottle, with a side tubulature near the bottom, was half-filled with hydrogen peroxide. Into the side neck was fitted a long graduated tube with a bend at right angles, which was to act as a pressure gauge. The brass tube containing the radium was passed through a tightly-fitting rubber cork, which was fixed firmly into the neck of the reagent bottle and so adjusted, that the radium was about three or four millimetres away from the surface of the liquid. In this way, any increase in the volume of the gas over the peroxide would produce a change in its pressure, and this change could be read by means of the pressure gauge. Figure 2 shows the apparatus.

These experiments were carried out in a photographic dark-room, so that there was no chance of the reaction being influenced by light.

¹ D'Arcy, *Phil. Mag.*, 1902 [VI], 3, 42.



360 cc. of hydrogen peroxide, of the strength mentioned above, were placed in the bottle just described, and put in the dark without being under the action of radium. The volume of gas enclosed over the liquid was 350 cc. The variations in pressure as observed by the pressure gauge were recorded for three hundred hours. After correcting this pressure for the variations due to changes of temperature and pressure, it was found that the pressure of the enclosed gas had not varied, showing that the peroxide had not suffered any decomposition during the time it was under observation.

Next an experiment was carried out, similar to that just described, except that the surface of the peroxide was bombarded by radium radiations. The increase in pressure was recorded from time to time, and the results obtained are tabulated in the following table:

TABLE I.

Time in hours.	Barometric pressure mm. Hg.	Temperature °C.	Height of liquid in manometer divisions, ¹	Increase in pressure of gas mm. Hg.	Corrected increase in pressure of gas mm. Hg.
0	761.0	19.1	145.0
7	762.01	18.8	149.9	0.5	1.7
15	762.11	18.0	157.3	1.1	4.4
30	764.10	18.8	160.2	1.4	4.1
40	763.90	19.2	165.0	2.0	2.7
50	764.01	18.0	156.0	1.0	5.8
75	761.39	17.1	151.3	0.6	6.4
100	767.11	16.6	155.5	1.0	10.9
118	764.31	16.8	163.0	1.9	10.0
142	766.01	17.9	167.0	2.2	8.4
165	764.02	18.0	162.1	1.9	6.7
200	765.13	18.0	160.1	1.4	6.8
219	764.99	18.1	158.4	1.3	6.3
238	764.41	18.1	155.0	1.0	5.6
265	760.99	19.5	163.0	1.9	0.8

¹ 20 scale divisions = 25 mm.

In the preceding table column five gives the changes in pressure of the gas in millimetres of mercury. These values have been calculated from the data in column four, the hydrogen peroxide having a density which is approximately one. Column six contains the values of column five after approximate corrections have been made for the changes due to variation in temperature and pressure; that is, these numbers represent the changes in pressure due to the increase of gas.

From these results, then, it is seen that the effect of radium on the solution of hydrogen peroxide is to decompose it. This decomposition, however, is small; for the increase in pressure corresponds only to a small increase in volume. In its behaviour towards hydrogen peroxide radium resembles light. It will be noticed that the pressure exerted by the gas, as given in the sixth column of the above table, after a time begins to decrease. The reason of this diminution in pressure will be considered later.

It is a well-known fact that the presence of finely divided solid matter or salts of the heavy metals slowly decomposes concentrated solutions of hydrogen peroxide, even at ordinary temperature. For this reason 10 cc. of $\frac{N}{10}$ solution of lead nitrate were added to 350 cc. of the dilute hydrogen peroxide used in these experiments. The addition of the lead nitrate to the peroxide caused the formation of a finely divided precipitate, the presence of which should also tend to decompose the solution. After making the necessary approximate corrections for changes in temperature and pressure, it was found that during the ten days the solution was under observation the pressure had not changed at all. Hence, it would seem that dilute solutions of hydrogen peroxide are not, or at most only exceedingly slowly, decomposed by the presence of finely divided solid matter or solution of lead nitrate.

An experiment similar to this was next carried out, with

the exception that the surface of the liquid was bombarded with radium rays. The results are given below in Table II.

TABLE II.

Time in hours.	Barometric pressure mm. Hg.	Temperature °C.	Height of liquid in manometer divisions. ¹	Increase in pressure of gas mm. Hg.	Corrected increase in pressure of gas mm. Hg.
0	759.99	20.8	142.0
9	759.90	20.8	160.5	1.7	1.7
12	759.71	21.2	167.0	2.3	1.7
15	759.41	21.4	169.5	2.5	0.8
19	758.74	21.6	165.0	2.1	0.1
23	759.21	21.8	156.5	1.4	1.5
33	759.20	21.1	141.5	0.1	1.1
36	759.30	20.6	142.8	0.1	0.4
41	759.21	19.6	136.6	0.5	2.3
48	759.41	19.1	138.0	0.4	3.9
58	759.53	17.4	95.0	4.3	4.3
63	759.91	17.4	167.0	2.3	6.3
67	760.10	17.4	108.0	3.3	5.3
73	765.31	17.4	90.0	4.8	6.3
82	767.90	16.8	89.0	4.9	9.9
87	769.18	17.6	104.0	3.5	9.0
92	767.20	18.5	123.0	0.7	9.0
100	766.17	18.0	170.0	2.6	13.2
104	764.39	18.0	208.0	6.1	15.7
109	758.55	18.0	252.5	10.1	16.7
115	754.54	18.5	305.0	14.1	17.9
120	758.52	18.4	352.5	19.3	24.9
130	758.63	18.7	483.7	31.2	36.0
136	758.63	18.7	489.2	31.8	36.6
153	761.05	18.6	358.2	19.8	27.5
160	761.52	19.6	394.5	23.2	26.9
167	761.09	19.0	387.0	22.5	28.4
177	760.99	17.4	343.0	18.6	28.3
188	761.26	17.4	389.0	22.8	32.5
194	761.84	17.2	413.0	25.0	35.5
202	765.17	17.0	391.0	23.0	35.6
216	764.69	15.4	299.0	14.4	30.9
225	762.70	12.6	238.0	8.8	31.5
236	761.75	14.2	299.0	14.4	34.2
240	761.23	14.2	334.0	17.6	37.1
255	769.36	15.6	379.0	21.8	41.5
265	761.91	14.8	354.5	19.5	35.7
276	763.30	11.6	274.5	12.2	37.9
294	765.86	11.8	286.5	13.2	39.6
304	767.02	12.3	303.0	14.8	40.4
314	752.34	12.8	638.3	46.4	63.7
321	752.34	13.6	711.3	52.3	67.4
324	753.86	13.6	681.0	49.6	65.2

¹ 20 scale divisions = 25 mm.

In column six of this table the increases in pressure due to the decomposition of the hydrogen peroxide are given, and on comparing these results with those given in Table I, it will be seen that the effect of the radium is to produce a much greater decomposition when lead nitrate is present than when it is not.

The Curies¹ have shown that the effect of radium radiations on oxygen is to transform it into ozone. It is to this cause that the decreases in pressure, corresponding to contractions in volume of the gas, observed in these experiments, have been attributed. Why there is this periodic change, the accumulative effect of which, as shown in Table II, is to enlarge the volume of gas, will have to be investigated more thoroughly before a suitable explanation can be given. On examining the gas which was over the liquid when the experiment was over, it was found that it contained 1.4 per cent. of ozone.

The foregoing experiments show that neither solutions of hydrogen peroxide (4.832 grams per litre), nor solutions of hydrogen peroxide in which lead nitrate is present undergo any decomposition in the dark; also that dilute solutions of hydrogen peroxide are slowly decomposed by radium, this decomposition being much more rapid when the solution contains lead nitrate and finely divided solid matter. Lastly, that ozone is produced by the action of radium on the oxygen present.

Action of Radium on Chloroform.

It is well known that the reason chloroform, CHCl_3 , does not give a precipitate with silver nitrate, is due to the fact that it is unionized. As there seems to be no absolutely undissociated substance, there is in chloroform, probably some few chlorine ions; these are so few that when they unite with the silver ions present in the system, the amount of silver chloride is very much too small to be visible. However, as soon as these chlorine ions are removed from the system as undissociated silver chloride, more of the chloroform dissociates in

¹ Loc. cit.

order to maintain the value of its solubility product, which must be exceedingly small. Thus the silver chloride accumulates very slowly and finally becomes visible. This explanation would seem to account for the appearance of silver chloride in a mixture of silver nitrate and chloroform a long time after mixing.

The following experiment was carried out to find whether chloroform could be ionized by radium to a sufficient extent, as to produce a visible amount of silver chloride when mixed with a solution of silver nitrate. About 50 cc. of chloroform which were found to produce no precipitate on mixing with a solution of silver nitrate, were placed in a wide-mouthed reagent bottle, with a capacity of about 125 cc. The brass tube containing the radium was passed through a tightly fitting rubber cork and fixed firmly into the mouth of the bottle. This solution was placed in the dark, and at the end of twenty-four hours it was shaken up with a few cc. of silver nitrate solution. After removing the water from the chloroform by allowing it to remain for a few hours over anhydrous copper sulphate, the liquid remaining possessed a milkiness which must have been due to the presence of silver chloride, thus proving that chlorine ions had been separated from the chloroform by the action of the radium.

Action of Radium on Amygdalin.

The laws of the action of light on glucosides, enzymes, toxins and antitoxins have been thoroughly investigated by Dreyer and Haussen,¹ who have shown that the effect of light on the glucosides is to cause them to break down with the formation of glucose. For the purpose of investigating the action of radium upon the glucosides, the most common one, amygdalin $C_{20}H_{27}NO_{11}$ was chosen. The amount of decomposition could readily be measured by estimating the amount of glucose formed.

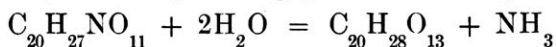
¹ C. R., 1907, 145, p. 564.

A saturated solution of amygdalin in water, was subjected to the action of radium rays for four days. At the end of that time part of the solution was tested with Fehling's solution for glucose. Not the least trace of glucose was found to be present. Another part of the solution was boiled with ammonium polysulphide, and after the excess of the latter had been removed by boiling, a few drops of dilute ferric chloride were added. As there was no change in colour hydrocyanic acid was inferred to be absent. Solutions of amygdalin were acted upon by radium for different lengths of time up to ten days, with the same result as above.

Although on boiling the solution of amygdalin, which had been under the influence of radium for a time, with a few drops of Fehling's solution, the copper was not reduced, thus showing the absence of glucose, the blue colour due to the copper, almost disappeared, a whitish or pale blue gelatinous precipitate was formed, and a fairly strong odour of ammonia was given off. If more than a few drops of Fehling's solution were added to the amygdalin, the blue colour did not disappear on boiling. When Fehling's solution was added to an ordinary solution of amygdalin, it was found that the same changes took place on boiling, except that the solution of amygdalin which had not been acted upon by radium, was not able to discolour as much Fehling's solution as was a solution that had been acted upon by radium. These changes must be due to some reaction taking place between the amygdalin and the Fehling's solution, or one or more of its constituents; these reactions are more complete when the amygdalin has been under the influence of radium for a time.

Amygdalin solutions were boiled with the constituents of Fehling's solution combined in all possible ways, but it was only when they were present so as to form Fehling's solution that the above results were obtained. When a solution of amygdalin was boiled with caustic potash alone, ammonia was given off but no precipitate was formed.

Liebig and Wöhler prepared amygdalic acid or glucomandelic acid, $C_{20}H_{28}O_{13}$ from amygdalin, by boiling it with baryta water, the change taking place in this way:—



This acid is a white crystalline substance which readily forms amorphous salts.

It is probable that the change taking place with Fehling's solution is one similar to this. The action of the potassium hydroxide is to form amygdalic acid and ammonia, and at the same time an insoluble salt of the former is formed with the copper, which is held in solution by the sodium and potassium tartrate in the Fehling's solution.

The decomposition of amygdalin by Fehling's solution does not take place unless the solution is boiled. However, if the solution of amygdalin is boiled with potassium hydroxide, cooled, and then a few drops of Fehling's solution added to it the bluish precipitate is formed.

A quantity of this precipitate was formed and washed free from amygdalin and Fehling's solution. When some of it was heated on a piece of platinum foil it charred, showing that it contained organic matter, and a greyish residue containing a carbonate and copper, but no sodium nor potassium was left behind.

From the foregoing facts it would seem that, on adding Fehling's solution to a solution of amygdalin and boiling, we have a change taking place like that observed by Liebig and Wöhler, resulting in the break down of the amygdalin. As a result of this decomposition the nitrogen of the amygdalin is changed to ammonia, and a bluish white precipitate, which is probably a copper salt of amygdalic acid, is formed. It is believed that the evolution of ammonia and the formation of the precipitate noted above, might be used for the detection of amygdalin. When the amygdalin has been under the influence of radium for a time, it is found this change is more complete.

Since solutions of glucosides are readily changed into glucose by hydrochloric acid, even in the cold, it was believed that if a solution of amygdalin were bombarded with radium radiations, this transformation might be accelerated.

The solutions of amygdalin used for this purpose had a concentration of ten grams per litre; the hydrochloric acid consisted of one volume of acid (sp. g. 1.2) to five volumes of water. The proportion of amygdalin to acid solution was ten to one.

The amount of decomposition was determined by titrating the glucose that was produced, with Pavy's solution, 25 cc. of which = 0.0151 gram of glucose $C_6H_{12}O_6$.

To determine whether the radium exerted any influence on the hydrolysis of amygdalin, the radium was placed over a vessel containing the acid solution of amygdalin, of the concentration mentioned above, and allowed to bombard the solution for a certain time; at the end of that time the amount of decomposition was compared with that of a similar solution that had not been acted on by radium. The vessels used to contain the solutions were ordinary wide-mouthed reagent bottles with a capacity of 125 cc. The tube containing the radium was securely fixed in a wooden block, which loosely fitted over the mouth of one of the bottles. Thus, by filling the bottle to a definite mark, the distance between the radium and the surface of the liquid was always kept the same. This distance was between two and three millimetres.

The following experiments were carried out in a photographic dark room, so that there was no chance of the reaction being influenced by light. The solution which was not to be acted on by radium was protected from the rays by a screen of lead, so placed that the solution would not be affected appreciably by the secondary rays set up in the lead.

Several experiments were carried out in this way, and the amount of glucose formed was estimated after different lengths of time. In the following table the numbers given in column two

denote the amount of amygdalin solution required to decolourise 2 cc. of Pavy's solution (25 cc.=0.0151 g. $C_6H_{12}O_6$), at the specified times after the instant of mixing. The temperature at which the action took place was $18 \pm 0^{\circ}.5$ C.

TABLE III.

Time in hours.	No. of cc. of Amygdalin solution required to decolourise 2 cc. of Pavy's solution when acted on by		No. of grams of glucose per 1 cc. of Amygdalin solution acted on by	
	RADIUM.	NO RADIUM.	RADIUM.	NO RADIUM.
19	11.54	12.08	0.000104	0.000099
30	13.39	12.29	0.000089	0.000097
48	14.77	12.28	0.000081	0.000097
66	16.27	12.39	0.000073	0.000097

From an examination of this table it will be seen that there is a striking difference between the behaviour of solutions of amygdalin acted upon by radium and those which have not been so influenced. For the solutions that have been bombarded with the radiations from radium, the content of glucose reaches a maximum and then falls off again; but with the solutions not under the influence of radium the amount of glucose present increases with time and then remains constant. An effect similar to this has been observed by the author¹ when acid solutions of potassium iodide made up with ordinary distilled water are allowed to decompose in the sunlight or dark; and when acid solutions of potassium iodide made up with pure water (conductivity 2.16×10^{-16}), are allowed to decompose under the influence of radium. In each of these cases the content of free iodine reaches a maximum and then gradually falls off again.

It would seem that the effect of the radium is to cause the glucose, in some manner, to change into some new product. In the case of the solution of amygdalin which has not been under

the influence of radium, where the content of glucose tends toward a constant asymptotic value, the simplest explanation is that the new product is not being formed, and we have an ordinary example of equilibrium between the amygdalin and its products of decomposition. If the new product is being formed two suggestions present themselves to account for the continued constancy of the glucose present: (1) that the rate of formation of the new substance is very small, but that in time the numbers in column five of the table would begin to drop also; (2) that the whole system reaches a state of equilibrium, and the amount of glucose will remain constant however long the time.

In order to ascertain whether the glucose was transformed into a simple substance or a complex one, by the action of radium, the effect of the latter on solutions of glucose in water and dilute hydrochloric acid, and on solutions of pure cane sugar in dilute hydrochloric acid was next studied.

Solutions of glucose and cane sugar of various strengths were experimented upon for different lengths of time, the change being measured by means of the polariscope. It was found that in no case was the change in the solution under the action of radium any different from that which was not influenced by radium, which seemed to show that the substance into which the glucose was changed in the amygdalin solution was not likely a simple one.

Action of Radium on Brass.

As has been mentioned before, the radium used in these experiments was enclosed in a narrow glass tube, which was held in the end of a hollow brass rod. The radium had been kept in this brass rod for about a year previous to these experiments. Some time after being placed there it was observed that the end of the brass rod, at which the radium was, began to be discoloured, and finally turned a deep grey. This discoloura-

tion was only at the surface next the air, for on scraping the surface of the rod with a knife, the inside was found to have the yellow colour of brass. While allowing the radium to act on hydrogen peroxide in the experiment previously described, where the brass rod was enclosed in an atmosphere of ozone, and air containing more oxygen than ordinary air, there was found on the part of the rod near the radium, a small quantity of this dark grey substance. Some of this was scraped off, care being taken not to remove any of the brass. On analyzing this substance it was found to contain only copper, there not being even so much as a trace of lead or zinc present. What has probably taken place is that the action of the radium on the brass in the presence of oxygen has slowly converted the copper of the alloy to copper oxide; the greater the amount of oxygen present the more rapidly the change takes place.

The results here given show that in many reactions the effect of radium is to accelerate that action already going on, and in the case of amygdalin and hydrochloric acid it may perhaps set up a new action of its own, besides accelerating the hydrolysis of the amygdalin into glucose, etc. Lastly the presence of amygdalin may be detected by boiling a solution supposed to contain it with a few drops of Fehling's solution and noting whether or not the odour of ammonia is given off.

The author's best thanks are due to Professor MacKay for the interest he has shown in these experiments.

DALHOUSIE UNIVERSITY, Halifax, N. S.

March 30, 1908.