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THE INFLUENCE OF RADIUM ON THE DECOMPOSITION OF  
HYDRIODIC ACID.\*—H. JERMAIN M. CREIGHTON, M. A.  
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(Communicated by Dr. E. Mackay, 25th October, 1907.)

The first mention of the influence of radiant energy of any kind on chemical reactions was made by William Cruickshanks<sup>1</sup>, who observed that hydrogen and chlorine combine under the influence of light. This particular reaction has been the source of many investigations, carried out by such men as Dalton<sup>2</sup>, Draper<sup>3</sup>, Bunsen and Roscoe, and, very recently, Mellor<sup>4</sup>, Bevan<sup>5</sup>, and Burgess and Chapman<sup>6</sup>. Of the numerous reactions affected by light, the following are some of the more important:—influence of light on silver salts, on the action of bromine and chlorine on metallic silver, on dyed colours, on enzymes in oxygen and hydrogen, on glass, on the oxidation of iodoform, action of oxygen on carbon bisulphide under the influence of light, the decomposition of hydrogen peroxide by light, effect of light on the combination of hydrogen and bromine, and the reaction between chlorine and benzene in the light.

\*Contributions from the Science Laboratories of Dalhousie University—[Chemistry]. Printed in advance in present part by permission of the Council of the Institute.

1. Nicholson's Jour., 1801, (1), 5, 202.
2. A New System of Chem. Phil., p. 300.
3. Phil. Mag., 1844, (iii), 25, 9: 1845, (iii), 26, 473.
4. Journ. Chem. Soc., 1904, 53.
5. Proc. Camb. Phil. Soc., 1902, (ii), 264-266.
6. Jour. Chem. Soc., 1906, 88, 1399.

Other forms of radiant energy whose effects on chemical action have been investigated are ultra violet light, Röntgen rays and radium radiations.

Only a comparatively small amount of work has been carried out on the effect of radium on chemical reactions. Hardy and Wilcocks<sup>1</sup> have investigated the oxidation of iodoform when acted on by Röntgen rays and by radium, and Hardy<sup>2</sup> has observed the coagulation of globulin under the influence of the latter. Becquerel<sup>3</sup> 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 Curies<sup>4</sup> have shown that the rays from radium change oxygen into ozone and discolour glass. Berthelot<sup>5</sup> cites the following cases: iodic acid is decomposed by radium rays and by light, with liberation of iodine, this change being much slower than that of iodoform; nitric acid gives off nitrous fumes when acted on by radium rays and by light. These, as far as I have been able to discover, are all the reactions that have been investigated up to the present time.

These investigations have been mainly of a qualitative nature, the quantitative side receiving very little attention. The following experiments were carried on with a view to finding out whether a quantitative examination of the change, if any, produced in hydriodic acid by the presence of radium would throw light on the part played by the rays in this decomposition. Hydriodic acid was chosen on account of its instability; and from its behaviour under the influence of light, it was believed that it would be affected by radium rays.

The effect of light on the decomposition of hydriodic acid has, in the last few years, been largely investigated. Pinnow<sup>6</sup>.

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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. Ber. d. deut. Chem. Ges., 1901, 34, 2528.

who has done a lot of this work, used acid solutions of potassium iodide for the production of hydriodic acid. He found that the best results are obtained when the solution of potassium iodide used has a concentration of 1 gram per litre. It was a solution of this strength that was used in all the following work. The hydriodic acid was set free from the iodide by a solution of sulphuric acid consisting of one part of acid (sp. g. 1.84) to five parts of water. The proportion of acid to iodide solution was one to eight.

The amount of oxidation was determined in the usual way, by titrating the liberated iodine with  $\frac{N}{1250}$  sodium thiosulphate solution.

It was found that the end point could be determined very quickly and accurately by highly illuminating the solution by means of an electric light placed behind it, and reflecting back the rays through the solution by placing a piece of white paper around the beaker on the opposite side.

The potassium iodide used was the chemically pure guaranteed reagent supplied by C. F. Kahlbaum.

By carrying out the titration in the above manner, the error was found to be about  $\pm 0.08$  cc. sodium thiosulphate solution.

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  $\beta$  and  $\gamma$  rays were used.

The starting point in the investigation was to determine whether radium exerted any influence on the oxidation of hydriodic acid. For this purpose, the radium was placed over a vessel containing the acid solution of potassium iodide, 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 upon by radium. The vessels used to contain the solutions were ordinary wide-mouthed reagent bottles, with a capacity of about 125 cc. The small glass tube

containing the radium was held in the end of a hollow brass rod, which was placed in a fixed position in a wooden block; this latter fitted into 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 millimeters.

These experiments were all 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 carried out in this way showed, at the end of twenty-four hours, that the decomposition in the solution acted upon by radium was greater than the decomposition in the other; but the excess varied in different trials from 15 per cent to 25 per cent. In order to obtain more concordant results for similar experiments, the temperature at which the reaction took place was kept constant for a series of measurements and it was found that this made a decided improvement in the agreement of the results. It was still found, however, that the differences in results under similar conditions were considerably greater than those due to experimental error. In order to see whether these differences were due to small errors in the mixing of the solutions, a large quantity of solution was prepared and divided into six equal parts of 225 cc. each. These were allowed to stand for twenty hours in the dark room, without radium, at a temperature of  $16 \pm 0.5^{\circ}\text{C}$ . At the end of that time the amount of decomposition, as measured by the number of cc. of titrating solution required, was found to be for the several portions, 5.38, 5.23, 5.41, 5.34, 5.07, 5.33, respectively. The lack of equality of these numbers shows that the irregularity is not to be accounted for in this way.

The influence of the impurities in the ordinary distilled water used in making up the solution was next investigated,

and it was found that when the water had a conductivity of  $2.0 \times 10^{-6}$  or less, at  $18^{\circ}\text{C}$ ., expressed in Kohlrausch's unit ( $\text{ohm}^{-1}, \text{cm}^{-1}$ )<sup>1</sup>, the agreement between the amounts of decomposition of several similar solutions was within the limits of experimental error.

The water used in the following experiments was prepared according to the method of Jones and Mackay<sup>2</sup>. The ordinary distilled water was doubly distilled. The steam from the first flask, which contained the water mixed with an alkaline solution of potassium permanganate, was bubbled through an acid solution of potassium bichromate in a second flask. Into the neck of the latter flask was thrust a block-tin condenser, and held there by means of a cork made of a mixture of plaster of Paris and asbestos. The water thus obtained has a mean conductivity of  $1.6 \times 10^{-6}$  at  $18^{\circ}\text{C}$ . It was kept in bottles which had been used several years for that purpose.

It was found that the purity of the water, as determined by the conductivity, played an important part in the rate of decomposition of the solution. The table below shows the results obtained when using water of two different grades of purity in the preparation of the solutions.

In this table, and all those that follow, the numbers given denote the amount of  $\frac{1}{1250}$  normal sodium thiosulphate solution required to titrate the free iodine content in the hydriodic acid solution at the specified times after the instant of mixing. The mixing was done in the dark room. In all cases the amount of hydriodic acid solution experimented upon was 50 cc.

The numbers in the following table are for the case where the mixture was left to stand in the dark room, and was not subjected to the action of radium or any other external action. The temperature was  $15 \pm 0.5^{\circ}\text{C}$ .

1. Kohlrausch und Holborn: *Leitvermögen der Elektrolyte*, 1898, p. 1.
2. *Zeit. phys. Chem.*, 1897, 22, 237.

TABLE I.

Time in hours.	No. of cc. of $\frac{N}{1250}$ $\text{Na}_2\text{S}_2\text{O}_3$ solution required in titration when hydriodic acid solutions were made up with	
	Water of conductivity ' $4.98 \times 10^{-6}$ .	Water of conductivity $2.16 \times 10^{-6}$ .
7	0.73	0.90
11	0.97	1.34
15	1.38	1.40
20	1.68	1.63
25	2.05	....
30	2.45	1.79
35	2.80	.. .
40	2.86	1.95
50	3.20	....
70	4.05	...
95	4.37	3.08
120	4.25	3.35
170	3.75	3.24
200	3.24	3.24
300	3.45	3.22
380	1.58	3.23
450	....	3.21
550	....	3.25
650	0.89	3.20
1100	....	3.24

From an examination of this table it will be seen that there is a striking difference between the behaviour of solutions made up with ordinary distilled water, and with water which has been more carefully purified. For the less pure water the content of free iodine rises to a maximum in about four days, and then gradually falls off again; but with the purer water the iodine content increases with the time for the first five days and then remains constant for the next six weeks during which

it was under observation. Similar hydriodic acid solutions made up with the less pure water were subjected to the influence of sunlight, and in that case also the iodine increases at first, reaches a maximum after some days, and finally disappears. Hence the effect of impure water is of the same nature whether the solution be left in the dark or acted on by the sunlight. It will be seen later that in certain circumstances radium has the same effect on solutions made up with pure water.

It would seem that the effect of the small amount of impurity in the water is to cause the iodine, by some sort of catalytic action to change into a third iodine product in addition to the hydriodic acid and free iodine, which alone we might at first expect. In the case of solutions made up with the purer water, where the iodine content tends towards a constant asymptotic value, as given in the third column of the above table the simplest explanation is that a third product is not being formed, and that we have there the ordinary equilibrium between the hydriodic acid, the hydrogen and the iodine. If the third product is still being formed, two suggestions present themselves to account for the continued constancy of the amount of free iodine present: (1) that the rate of formation of the third product is very small, but that in time the numbers in the last column of the table would begin to decrease also; (2) that the whole system reaches a state of equilibrium, and the iodine content will be constant however long the time. The former suggestion is the more probable one, since it is likely that by a more careful distillation of the water we have not got rid entirely of the cause of the trouble, but only reduced it in amount.

This, however, is not the only effect of the impurity in the water; it also accelerates the rate of accumulation of iodine. This is evident from the fact that the maximum value reached in the case of the less pure water is greater than the asymptotic value approached in the case of the more pure sample. As it

was found that the rate of production of free iodine was much affected by temperature, it was felt that an answer to the question of whether radium radiations had a specific action of their own on hydriodic acid, or only changed in degree the action going on in their absence, was to be looked for from a study of the action at different temperatures both with and without the presence of radium. Further efforts at an explanation of what is the action of external agencies such as impurity, light, Becquerel rays, etc., will therefore be deferred until the experiments on the effect of temperature on solutions with and without radium have been detailed.

The following table contains the results obtained with water of a high degree of purity at a temperature of 24°C., both with and without radium. A new sample of 50 cc. of hydriodic acid solution was taken for each period of time shown.

TABLE II.

Time in hours.	No. of cc. of $\frac{N}{1250}$ $\text{Na}_2\text{S}_2\text{O}_3$ solution required in titration when decomposition of hydriodic acid solution takes place in the dark in the presence of			
	No radium.		Radium.	
	Observed $y$	Calculated from $y = a(1 - e^{-bt})$ $a = 1.54, b = 0.175$	Observed $y$	Calculated from $y = a(1 - e^{-bt})$ $a = 2.10, b = 0.175$
2	0.45	0.45	0.58	0.62
3	0.65	0.63	0.85	0.86
5	0.92	0.90	1.25	1.23
7	1.10	1.09	1.51	1.48
10	1.23	1.27	1.73	1.73
12	1.27	1.35	1.77	1.85
16	1.38	1.45	1.94	1.98
21	1.52	1.50	2.01	2.05
38	1.56	1.54	2.09	2.10

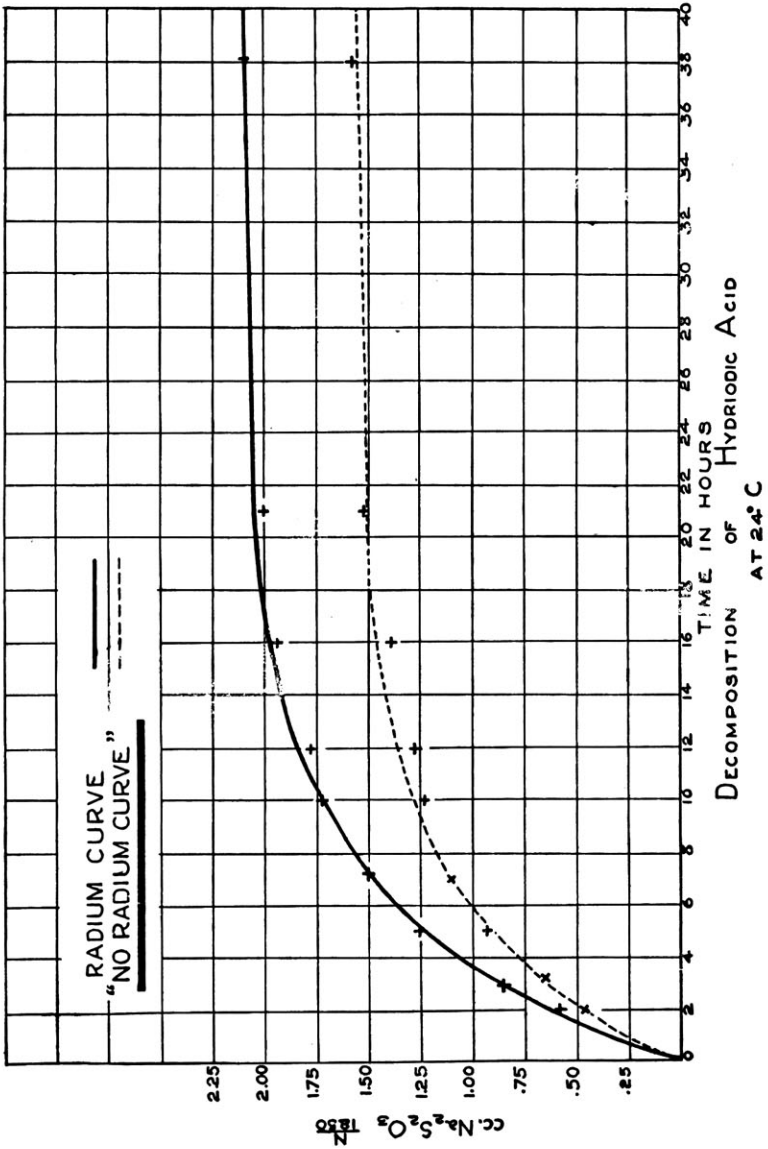


In the third and fifth columns of Table II. are added numbers calculated from the equation

$$y = a (1 - e^{-bt})$$

with the values of  $a$  and  $b$  there given, to show how well the observations are represented by curves of this type. These calculated curves are plotted in figure (1), the amounts of sodium thiosulphate solution being represented as abscissae. The observed values are marked and lie remarkably well on the curves. The similarity of these two curves seems to show that with pure water, at this temperature, the action of radium is of the same nature as that which goes on without it in the dark, but is greater.

FIG. 1.



If now, in the reaction under investigation, we assume that the hydriodic acid breaks down into iodine, and that this in turn breaks down into a third substance, then we have a case which is similar to the successive changes which take place in the break down of radium. Rutherford<sup>1</sup> has shown that if in such a change as this  $n$  is the amount of any substance A, in this case hydriodic acid, initially present, then the amount of B, in this case free iodine, at any time is given by the equation

$$y = \frac{n\lambda_1}{\lambda_1 - \lambda_2} (e^{-\lambda_2 t} - e^{-\lambda_1 t}) \dots \dots \dots (1)$$

where  $\lambda_1$  and  $\lambda_2$  represent the rates of change of A into B and of B into C, respectively, where C is the third product.

Assuming that this third product is formed, there seem to be three probable ways in which the radium may act.

(1) The production of iodine is accelerated and also the production of the new product into which the iodine is changed.

(2) The production of iodine is unaffected, but that of the third product retarded.

(3) The production of the iodine is accelerated, while the production of the third product is retarded.

Of these three cases the two latter seem to be the least probable.

Let us apply equation (1) to the results of observation at 24°C. If the second change is very slow or zero, that is, if  $\lambda_2$  is negligible, the amount of free iodine at the end of time  $t$  would be given by the equation

$$y = n (1 - e^{-\lambda_1 t}) \dots \dots \dots (2)$$

Solving this equation for  $\lambda_1$ , we get

$$\lambda = \frac{\log n - \log (n - y)}{t \log_{10} e} \dots \dots \dots (3)$$

Substituting in this equation values of  $t$  and  $y$  obtained from columns 1, 2, and 4 of Table II, we derive for  $\lambda$  values which show a very satisfactory agreement, as is seen in the following table :

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1. "Radioactivity," p. 332.

TABLE III.

Time in hours.	No radium curve . $n=1.54$		Radium curve . $n=2.10$	
	Amt. $\text{Na}_2\text{S}_2\text{O}_3$ $y$	Rate of change. $\lambda$	Amt. $\text{Na}_2\text{S}_2\text{O}_3$ $y$	Rate of change. $\lambda$
2	0.45	0.173	0.58	0.162
3	0.65	0.183	0.85	0.173
5	0.92	0.182	1.25	0.181
7	1.10	0.719	1.51	0.181
10	1.23	0.160	1.73	0.174

This justifies us in supposing that at 24°C., both with and without radium, there is no third product being formed from the iodine; and the numbers given in columns three and five of Table II were calculated from equation (2). As was pointed out before, the action of radium serves merely to accelerate the action which goes on in its absence.

In order to see if more light would be thrown on the action of the radium the decomposition of hydriodic acid was observed at other temperatures.

The reaction was next observed at 12°C., and the results are given in the following table:

TABLE IV.

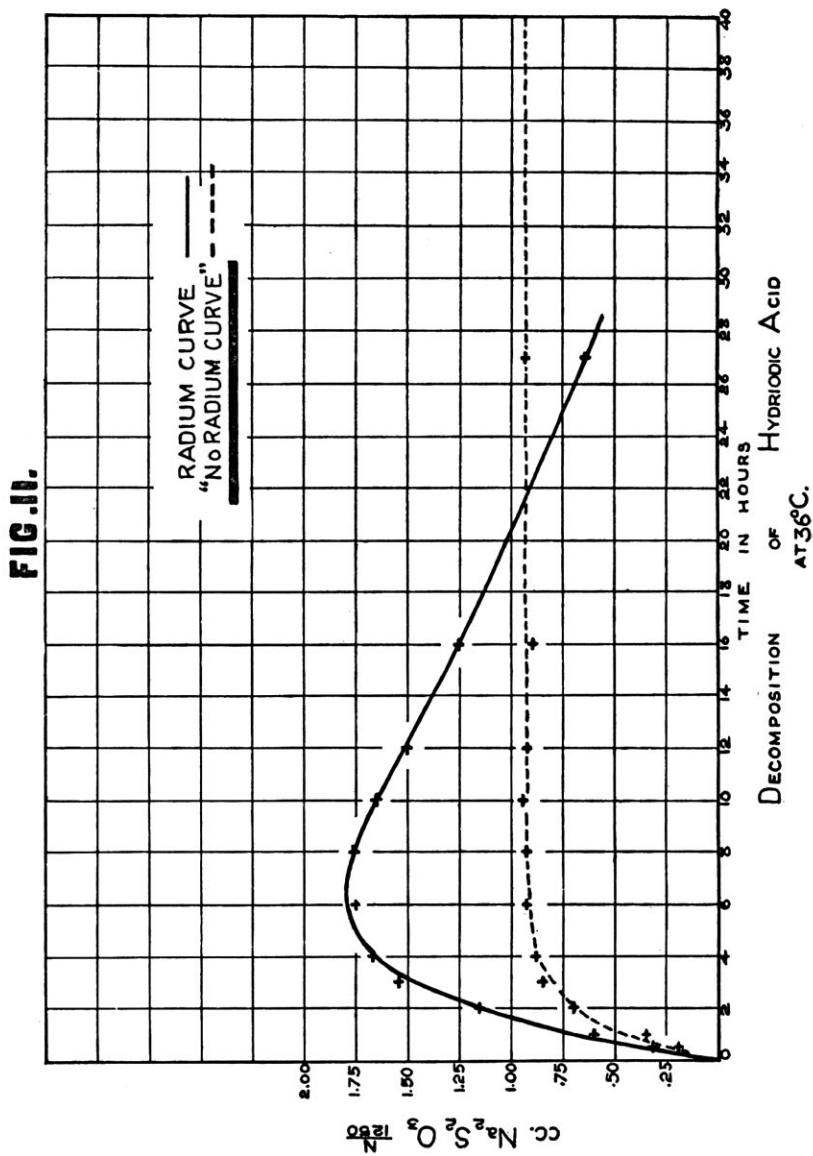
Time in hours.	No. of cc. of $\frac{N}{1250} \text{Na}_2\text{S}_2\text{O}_3$ solution required in titration when the decomposition of hydriodic acid takes place in the dark in the presence of			
	No radium.		Radium	
	Observed $y$	Calculated from $y = a(1 - e^{-bt})$ $a = 1.92, b = 0.07$	Observed $y$	Calculated from $y = a(1 - e^{-bt})$ $a = 2.90, b = 0.07$
2.5	0.30	0.31	0.49	0.46
8.0	0.75	0.83	1.15	1.25
10.0	0.95	0.96	1.43	1.46
18.0	1.47	1.37	2.15	2.08
30.0	1.69	1.69	2.55	2.55

The curves for these numbers are similar in form to those for 24°C. The only difference between the behaviour at this temperature and that at 24°C. is that at the former the decomposition of the solution is much slower, and the equilibrium values consequently much longer in being reached. The effect of radium is again apparently only to increase the action in degree, but not to change it in type. Here, too, as at 24°C., there is probably no third product being formed from the iodine. The reaction was next observed at 36°C., and the following table shows the results obtained :

TABLE V.

Time in hours.	No. of cc. of $\frac{N}{1250}$ $\text{Na}_2\text{S}_2\text{O}_3$ solution required in titration when the decomposition of hydriodic acid solution takes place in the presence of			
	No radium		Radium	
	Observed $y$	Calculated from $y = a(1 - e^{-bt})$ $a = 0.92, b = 0.70$	Observed $y$	Calculated from $y = a(e^{-bt} - e^{-ct})$ $a = 3.3, b = 0.06,$ $c = 0.31$
0.5	0.18	0.27	0.30	0.38
1	0.35	0.46	0.60	0.69
2	0.70	0.69	1.15	1.15
3	0.85	0.81	1.50	1.46
4	0.88	0.87	1.65	1.64
6	0.93	0.91	1.75	1.79
8	0.92	0.92	1.75	1.75
10	0.93	0.92	1.65	1.64
12	0.91	0.92	1.50	1.52
16	0.90	0.92	1.25	1.24
27	0.93	0.92	0.65	0.65

The curves formed from these numbers are given in figure 2.



At this temperature it is seen that the maximum is quickly reached in the case of the solution under the influence of the radium ; and the effect due to the second reaction, the supposed changing of the iodine into a third substance, is soon noticeable. On the other hand, the curve for the solution not affected by radium resembles the curves for both radium and no radium at lower temperatures, but it would seem probable that in this case the time taken to reach the maximum is shorter. In this case also there is therefore no measurable formation of the third product. A comparison of the no radium curves for 12°, 24° and 36°C will show that with a rise in temperature the rate of decomposition of hydriodic acid increases, while the maximum amount of iodine in solution is less and the time taken to reach this maximum shorter. The same is true for the radium curves at 12° and 24°C.

If the theory previously stated of what is taking place be correct, the general equation (1) should be the equation of the radium curves for 36°C.

Rutherford<sup>1</sup> has shown that the smaller of the two quantities  $\lambda_1$  and  $\lambda_2$  is given by the latter part of the downward curve. The equation of this part of the curve is then of the form

$$y = n \cdot e^{-\lambda t} \dots \dots \dots (4)$$

Accordingly, from the observed values of  $y$  at 12, 16 and 27 hours,  $n$  was found to be 3.3 and  $\lambda_1$  to be 0.06. By finding the differential of equation (1) with regard to time and equating it to zero, we find that the maximum occurs at a time  $T$ , given by the equation

$$\lambda_1 e^{-\lambda_1 t} = \lambda_2 e^{-\lambda_2 t} \dots \dots \dots (5)$$

Putting for  $t$  the value 6.6 found from the curve, and for  $\lambda_1$  its value 0.06, we find  $\lambda_2$  to be 0.31. The numbers calculated from equation (1) with these values of the constants are given in the last column of Table V, and the agreement with the observed values falls well within the limit of experimental error.

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1. Loc. cit., p. 343.

Since for no radium at 36°C.,  $\lambda_1$  was found to be 0.70, and  $\lambda_2$  was zero (or very small), we see from the foregoing results that the influence of the radium at this temperature is to decrease the rate of decomposition of the hydriodic acid into iodine, and to increase the second action considerably, namely the transformation of the iodine into the third compound.

It is an easy matter to determine when the amount of hydriodic acid is half gone. If  $n$  is the amount of hydriodic acid initially present and  $P$  is the amount present at any time  $t$ , then

$$P = n e^{-\lambda_1 t}$$

Calling  $T$  the time taken for half of the hydriodic acid to be transformed, we have

$$\frac{1}{2} = e^{-\lambda_1 t}$$

$$\text{whence } T = - \frac{\log_e 0.5}{\lambda_1}$$

Substituting the values of  $\lambda$  obtained with no radium for 24°C. and 36°C. in this equation, we find that it takes about 384 hours at the former temperature and about 17 hours at the latter for half the amount of hydriodic acid to be decomposed into iodine.

#### *Effect of Temperature.*

In order to show the effect of temperature alone, both when the solution is under the influence of radium and without it, the reaction was allowed to proceed for ten hours at various temperatures. The results were as follows:



TABLE VI.

Temperature.	No. of cc. of $\frac{N}{1250}$ $\text{Na}_2\text{S}_2\text{O}_3$ solution required in titration when the decomposition of hydriodic acid takes place in the dark in presence of		Difference.
	No radium.	Radium.	
0	0.20	0.78	0.58
4	0.45	1.02	0.57
8	0.68	1.21	0.53
12	0.95	1.43	0.48
16	1.20	1.73	0.53
20	1.25	1.75	0.50
24	1.23	1.73	0.50
36	0.93	1.65	0.72
	Mean of all Differences except that for 36°C. . .		0.53

If these numbers are plotted it is seen that the curves are straight lines below 16°C. If the latter are produced backward they will cut the axis of temperature at about  $-12^\circ\text{C}$ . and  $-3^\circ\text{C}$ . for the radium and no radium curves respectively. At these temperatures there should be no decomposition unless the curves should become asymptotic, and, considering the steepness of the curves at  $0^\circ\text{C}$ ., this would not seem probable for the "no radium" curve at least. Of course it was out of the question to keep the solution at  $-12^\circ\text{C}$ . on account of its freezing, but a solution could easily be kept at  $-3^\circ\text{C}$ . for a time.

This temperature ( $-3^\circ\text{C}$ .) was easily obtained by placing the solution in a bath of very dilute alcohol, which was surrounded by a mixture of salt and snow. It required but little attention to keep this bath at a temperature of about  $-3^\circ\text{C}$ . to  $-4^\circ\text{C}$ .

It was found at the end of ten hours that the decomposition in a solution not under the influence of radium, and kept at a temperature of  $-3^\circ\text{C}$ . during that time, was equivalent to 0.19 cc. sodium thiosulphate. Hence the curves at  $0^\circ\text{C}$ . must cease to be straight lines, and begin to run asymptotically toward the axis of temperature.

From this work on the effect of temperature we are again led to conclude that the radium intensifies the action that is already going on.

*Effect of  $\gamma$  Rays Alone.*

Hardy and Wilcocks<sup>1</sup> have shown that the  $\gamma$  rays from radium accelerate slightly the decomposition of iodoform, but that the acceleration is small as compared with that due to the  $\beta$  rays. In order to determine whether the  $\gamma$  rays behave in the same way upon the hydriodic acid reaction, the rays from the radium were made to pass through 6 millimetres of lead before entering the solution. This thickness of lead is sufficient to absorb all but the fastest  $\beta$  rays, and does not appreciably absorb the  $\gamma$  rays. The reaction was first allowed to go on for ten hours at 24°C, when the amount of free iodine was found to be equivalent to 2.10 cc. sodium thiosulphate solution.

For the sake of comparison the results for ten hours are here grouped :

No radium for 10 hrs. at 24°C. . . . .	1.23	cc.	$\frac{N}{1250}$	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	solution
$\beta$ and $\gamma$ rays           "           "	. . . . .1.73	"	"	"	"
$\gamma$ rays                   "           "	. . . . .2.10	"	"	"	"

At first this result seems to disagree with that obtained by Hardy and Wilcocks. Indeed it does not seem reasonable that the  $\gamma$  rays, whose energy is much less than that of the  $\beta$  rays, should accelerate the decomposition more than the latter. Closer consideration, however shows that the disagreement is only apparent and that the result is in accordance with the above theory of the break down of hydriodic acid.

For if, as we have supposed, there are two successive reactions taking place, both of which are accelerated by the influence of radium, then since it has been shown that the second one of these is the more influenced, it is quite probable that when the energetic  $\beta$  rays are absorbed and not allowed to enter the solution, the second reaction is relatively retarded, and so we have the amount of free iodine in the solution increased. If this is what is happening, then for a few hours after the

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1. Loc. cit.

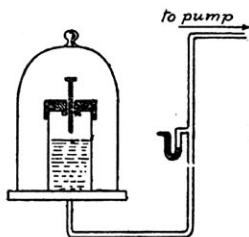
beginning of the reaction, before the second reaction begins to make itself felt, we should expect to find that the amount of iodine set free is less when the solution is acted upon by  $\gamma$  rays, than when it is acted upon by  $\beta$  and  $\gamma$  rays. At the end of three hours, when the solution had been kept at  $24^{\circ}\text{C}$ ., the decomposition was found to be as follows :

No radium for 3 hrs. at $24^{\circ}\text{C}$	...	0.65	cc.	$\frac{\text{N}}{1250}$	$\text{Na}_2\text{S}_2\text{O}_3$	solution
$\beta$ and $\gamma$ rays	"	"	...	0.85	"	"
$\gamma$ rays	"	"	...	0.72	"	"

*Influence of Sunlight and Radium in the Absence of Oxygen.*

If a hydriodic acid solution such as was used in the preceding experiments be entirely freed from occluded air, and placed in a tube from which all the air has been removed, it was found that this tube could be placed in the sunlight for any length of time, without the solution showing any decomposition. In order to remove all occluded air before being sealed off, the solution was kept in a vacuum in the dark for twenty-four hours ; for otherwise it is found that extremely minute quantities of dissolved air will slightly decompose the hydriodic acid.

The same experiment was then tried with radium, instead of sunlight. In order to keep the solution under a vacuum for two or three days, without sealing up the radium in a tube with the solution, the vessel containing the solution with the radium was placed under a bell jar on a brass plate, connected by a glass tube to a "Geryk" vacuum pump. The joint between the



bell jar and the brass plate was made perfectly tight by sealing it with a preparation made by heating together equal parts of pure india rubber, paraffin, and vaseline. When the vacuum was made this tube was sealed off from the pump. A delicate manometer connected with the jar, showed no change

in vacuum at the end of several days. It was found that the radium also produced no effect. The experiment was tried at room temperature only.

*Summary.*

1. When prepared with very pure water a hydriodic acid solution decomposes in the dark, reaching an equilibrium value. (Experiments made up to 36°C.)

2. Ordinary distilled water contains impurities producing some catalytic action which accelerates the decomposition of hydriodic acid solution in the dark, at the same time introducing another reaction, which causes the amount of free iodine to reach a maximum value and then fall off indefinitely. (Experiments made at 15°C. only.)

3. At any temperature up to 24°C, more iodine is liberated in a given time from a solution of hydriodic acid in the dark, under the influence of radium, than from one that is not so influenced.

4. When the experiment is tried at 36°C. this last statement is only true up to 24 hours; for whereas the amount of free iodine with no radium reaches an equilibrium value, with radium it reaches a maximum and then falls off indefinitely.

5. At 36°C. radium seems to cause the formation of the same third product which impurity in water produces at low temperature.

6. In general, increase of temperature tends to increase the amount of free iodine at any time, whether radium is used or not.

7. The  $\gamma$  rays alone cause more iodine to be free than do the  $\beta$  and  $\gamma$  rays together. (Experiments made at 24°C. only.)

8. Neither sunlight nor radium causes decomposition of hydriodic acid solution in absence of oxygen. (Experiment made at room temperature only.)

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