

THE BEHAVIOUR OF SOLUTIONS OF HYDRIODIC ACID IN LIGHT  
IN THE PRESENCE OF OXYGEN.\*—By H. Jermain M.  
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It is well known that solutions of hydriodic acid and acid solutions of potassium iodide readily change into free iodine and water. These reactions are accelerated by light, and also, as the author<sup>1</sup> has shown, by radium. While investigating "the influence of radium on the decomposition of hydriodic acid" the author<sup>2</sup> observed that the iodine set free by the oxygen increased with the time, reached a maximum and then gradually fell off again, under certain conditions. It was also observed that solutions of iodine placed in the sunlight slowly became colourless. It was to try to account for the disappearance of this iodine that this investigation was undertaken.

The hydriodic acid used in these experiments, was set free from solutions of potassium iodide by means of a sulphuric acid solution consisting of one volume of acid (sp. g. 1.84) to five volumes of water. The solutions of potassium iodide used had a concentration of 1 gram per litre. 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.

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

<sup>1</sup> Creighton, Proc. and Trans. N. S. Inst. Science, vol. xii, 1, 1.

<sup>2</sup> Loc. cit. Also Creighton and Mackenzie, Amer. Chem. Jour., 1908. 39, 4 (April).

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

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

As has already been stated, the iodine in solutions of hydriodic acid diminishes under certain conditions; in the case where the hydriodic acid is placed in the sunlight the iodine entirely disappears in time. If there was a new substance being formed, it was felt that its nature could best be ascertained from a study of the change under the action of sunlight, as this was the most easy to control and by far the most rapid.

As a starting point in this investigation, a large quantity of solution was made up in the manner previously described, and placed in a window where it would receive the most sunlight. Portions of 50 cc. of this solution were titrated with sodium thiosulphate from day to day and thus the variations in the content of free iodine were established.

On account of the reaction being a reversible one and its point of equilibrium being changed by light, the numbers in the following table are given for the days which were of about the same degree of brightness.

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 the decomposition of hydriodic acid takes place in sunlight.	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 sunlight.
24	46.31	552	20.42
72	58.42	720	18.55
120	64.42	840	16.62
144	58.93	888	14.26
189	52.14	960	11.80
236	49.97	1056	10.74
288	45.14	1152	6.41
408	44.12	1272	3.12
456	28.55	1368	0.46
504	23.41	1392	0.00

From this table it is again seen that the iodine content reaches a maximum very rapidly and then slowly falls off again and finally disappears. During the last two hundred hours the disappearance of the iodine is relatively rapid. In this experiment it was found that the disappearance of the iodine was due, in part, at least, to evaporation; accordingly, to see whether evaporation was responsible for the whole change, and at the same time to determine how much light influenced this change of iodine, the following experiment was carried out.

300 cc. of an acid solution of potassium iodide, such as had been used already, were put in each of two reagent bottles, one amber colour, the other clear; these were closed, and about every twelve hours the air that was over the liquid was passed through U-tubes containing a solution of potassium hydroxide (sp. g. 1.27), by means of an aspirator.

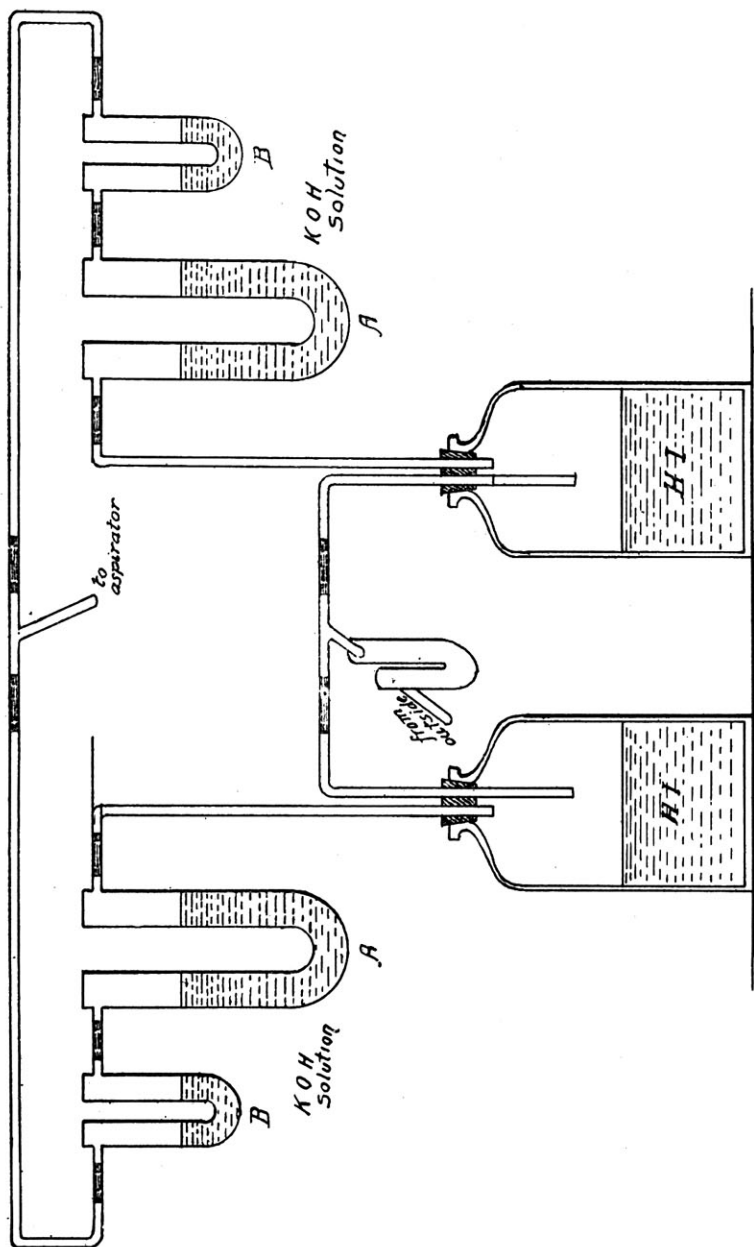


Fig I

The air thus removed was replaced by air from outdoors, which first passed through a U-tube containing potassium hydroxide. The air, after passing through this solution of potassium hydroxide divided, and half went to one solution and half to the other. After passing over these solutions it went, as stated, through the potassium hydroxide in the U-tubes, A and B, and then met in a common tube leading to the aspirator. By these means it was very easy to pass the same quantity of air over each solution. A diagram of the apparatus is given in Fig. 1. After the last trace of the iodine had disappeared the amount absorbed could easily be estimated. The use of the second smaller U-tubes marked B in the diagram was to make sure of the complete absorption of the iodine.

After the solution had been exposed to the action of sunlight for seven weeks, the solution in the bottle that was not coloured, became colourless. The solution in the amber coloured bottle still contained considerable quantity of iodine, and it was not for nearly another seven weeks that its colour entirely disappeared. This shows that the change of the iodine is accelerated by light, and that its loss cannot probably be totally accounted for by evaporation. On examining the U-tubes containing the caustic potash solution, it was found that the first one, A, contained iodine, while there had been none absorbed in the second smaller tube, B, showing that no escape of iodine had taken place.

The amount of iodine carried away by the air and absorbed by the solution of potassium hydroxide was next determined.

When iodine is absorbed in potassium hydroxide, there is formed five molecules of potassium iodide to one of iodate. The solution of hydroxide was acidified with sulphuric acid; and as some of the iodide might have oxidised to iodate, a little iodide was added to ensure complete decomposition of the iodate, then a few cc. of starch solution added, and the liberated iodine determined by means of sodium thiosulphate solution.

The potassium hydroxide solution from the U-tubes was diluted to 200 cc. 45 cc. of this solution were acidified and titrated with  $\frac{N}{10}$  sodium thiosulphate solution, of which 1.53 cc. were required to remove the blue colour due to the iodine. From this data it may be shown that the 200 cc. of hydroxide, therefore, contain 0.0864 gram of iodine. Only one-sixth of this iodine was present as iodate in the potassium hydroxide solution, that is 0.0144 gram. The quantity of iodine as iodide was estimated by oxidising it to iodate by means of potassium permanganate solution; 1 cc. of this solution = 0.0056 gram of permanganate. 25 cc. of the solution of potassium hydroxide which had been diluted to 200 cc. was acidified slightly with sulphuric acid and then made alkaline with potassium carbonate. The permanganate solution was then added until the liquid became slightly pink. In this titration 4.40 cc. of the potassium permanganate solution, corresponding to 0.0246 gram of potassium permanganate, were required to oxidise the iodine. It will readily be seen that this amount of potassium permanganate has been used in oxidizing 0.0098 gram of iodine. Therefore, the amount of iodine in the potassium hydroxide solution as iodide was eight times this amount, or 0.0784 gram. Hence, the total amount of iodine lost by evaporation from the iodine solution and absorbed by the potassium hydroxide solution was,

$$\begin{array}{r}
 0.0144 \text{ gram iodine as iodate} \\
 0.0784 \text{ " " " iodide} \\
 \hline
 0.0928 \text{ " " absorbed.}
 \end{array}$$

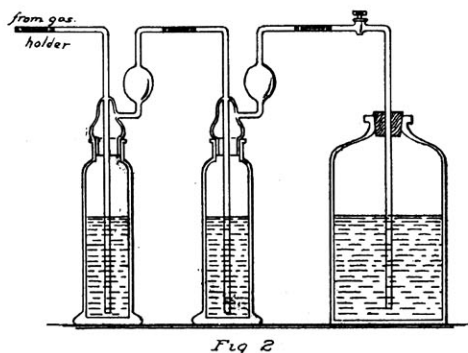
In this experiment 300 cc. of iodide solution (conc. 1 gram per litre) which contained 0.2293 gram of iodine, were used. From these numbers it will be seen that the loss by evaporation was 40.47 per cent., which leaves still sixty per cent. to be accounted for.

Before leaving this experiment it would be well to mention here that after all the iodine had disappeared from the solution

it still possessed a slight colour, not unlike the colour produced when Nessler's solution is added to a solution containing a minute quantity of ammonia. About a week after the last of the iodine had disappeared, this colour went also. In all solutions of hydriodic acid, where the iodine disappears, this colour was observed.

Although it seemed absolutely certain, from the fact that the second U-tube, B, in the above apparatus contained no iodine, none of it could have escaped out of the latter into the atmosphere, yet the objection arose that as the gas inside the bottles was taken out, carrying with it iodine, some of the iodine, although very unlikely, might have escaped. It was to overcome this objection that the experiment to be described was carried out.

500 cc. of acid potassium iodide solution were placed in a



reagent bottle provided with a tightly fitting rubber cork, through which passed a glass tube provided with a stop-cock. This glass tube went almost to the bottom of the liquid as shown in Fig. 2. This tube was connected

with a gas holder containing oxygen under pressure, the gas from which was first purified and dried, by passing through wash bottles containing sodium bicarbonate and concentrated sulphuric acid, before being allowed to enter the iodide solution.

The stop-cock was opened, the rubber cork loosened, and the air in the bottle displaced by oxygen. The rubber stopper was then tightly fitted, the oxygen in the bottle allowed to attain the same pressure as that in the holder, and the stop-cock closed.

At the end of twenty-four hours on opening the stop-cock again, a large quantity of oxygen was found to bubble through the solution, showing that some of the oxygen there had been used up during the twenty-four hours. Every day as much oxygen as possible was forced into the bottles containing the solution, until at the end of about nine weeks, the solution had lost all its colour, with the exception of the slight peculiar colour mentioned previously. Some of the solution was drawn off and tested for iodine and iodides, but not the least trace of either was found to be present. The passage of oxygen into the solution was continued with the result, that at the end of another week, the slight colour possessed by the solution entirely disappeared. During this time it was roughly estimated that not less than twenty-five litres of oxygen, at the ordinary temperature of the laboratory and a pressure somewhat above the normal, were passed into the iodide solution.

On the foregoing grounds then, it is not unreasonable to suppose that the iodine is being transformed into some oxygen compound, and that this transformation is accelerated by light.

Creighton and Mackenzie<sup>1</sup> have shown in the case of solutions of hydriodic acid acted upon by radium, where the iodine content after a time begins to diminish, it is very probable it is the hydriodic acid that is transformed and not the iodine itself, thus lessening the content of free iodine by upsetting the equilibrium between the two substances. On account of the similarity between the two cases, it is possible that this is the manner in which the change takes place here.

The colourless solutions from which the iodine had disappeared were now examined. It was found that these solutions contained no iodide, but, however, a small quantity of iodate. If these solutions were allowed to stand for a few weeks after becoming colourless, before testing, there could not be obtained the slightest trace of iodate. These facts would seem

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<sup>1</sup> *Loc. cit.*



to show that the process of the change is one of oxidation, through the different oxygen compounds of iodine. The amount of iodine as iodate in the solution into which oxygen was passed, just after the last trace of iodine had disappeared, was found to be 0.0000372 gram per cc. or the 500 cc. started with would contain 0.0186 gram; that is, 4.87 per cent. of the original amount of iodine.

It is evident then that the amount of iodate present in the solution will be greatest just after the solution becomes colourless; that is, never very much greater than 4.87 per cent. This will readily be seen from the consideration that no appreciable amount of iodate could exist, while there was any potassium iodide or hydriodic acid present in a solution containing sulphuric acid. Also it has been shown that the amount of iodate decreases with time, after the solution loses its colour.

It seemed a not unlikely explanation that the iodine might be changed into periodates. It would appear a perfectly natural process for the hydriodic acid to be oxidised to iodic acid, possibly through the intermediate formation of hypiodous acid, and this quickly transformed to some of the periodic acids. Of course, there could not, and need not, be any appreciable amount of these intermediate substances present at any time. In order to test this explanation the solution was examined for periodates.

On adding a solution of silver nitrate to the acidified solution a slight milkiness appeared. 0.0062 gram of this precipitate yielded on heating 0.0031 gram of metallic silver, which amount corresponds to the quantity of silver contained in silver dimesoperiodate,  $\text{Ag}_4\text{I}_2\text{O}_9 + 3\text{H}_2\text{O}$ . However, it could not be this substance, as the solution failed to yield iodine on reduction.

Since from the manner in which the iodine disappeared, it was believed that the iodine must have changed to some oxygen compound, the effect of strong reducing agents were tried on the solution. Zinc dust was added to the acid solution and

allowed to act for a couple of hours; portions of the residue from the solution were heated with potassium cyanide and powdered charcoal, and with powdered magnesium; and lastly some of the residue was heated in a current of hydrogen to such a high temperature, that the sodium sulphate was reduced to sulphide. In neither of these instances was the slightest trace of iodine obtained.

As it was thought that an analysis of the solution might throw some light on the problem, the following determinations were undertaken.

80 cc. of the colourless solution that had been acted on by pure oxygen, and which, therefore, must have contained all the iodine originally in it, were exactly neutralized with potassium carbonate and evaporated to dryness. The residue after being dried at  $110^{\circ}$  for an hour weighed 8.0530 grams. This residue was used for the analysis, and the only substances that it could contain besides the iodine, were potassium, and sulphuric acid in the form of sulphate, (it was proved that there was no carbonate present).

The amount of sulphuric acid ( $\text{SO}_4''$ ) was determined by precipitating with barium chloride. The following are the results obtained:

(1)	1.4914	grams residue yielded	1.9813	grams $\text{BaSO}_4$
(2)	1.4914	“ “ “	1.9842	“ “
			1.9827	
		mean	1.9827	

This weight of barium sulphate corresponds to 0.8168 gram of  $\text{SO}_4''$ , or to 54.76 per cent. of the residue used.

The potassium was estimated by precipitating as double potassium-platinum chloride. This precipitate after being thoroughly dried, was heated with oxalic acid and reduced to a mixture of metallic platinum and potassium chloride,

Pt + 2KCl. From this the amount of potassium was determined. It was found that:

(1)	0.4890 gram of residue yielded	0.9674 gram	Pt + 2KCl.	
(2)	0.4890 " " "	0.9610 " "	" "	" "
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	mean	0.9642	" "	" "

This corresponds to 0.2193 gram of potassium, which is 44.83 per cent. of the residue used.

These results are arranged in the following way so as to be more obvious:

	Theoretical composition of K <sub>2</sub> SO <sub>4</sub>	Composition of residue examined.	
		(1) High results.	(2) Low results.
Potassium . . . . .	44.87%	44.98%	44.68%
Sulphuric acid (SO <sub>4</sub> ) . . . . .	55.13%	54.81%	54.73%
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	100.00%	99.79%	99.41%

When the weights of the substances corresponding to these percentages are calculated for 1.4914 grams there is obtained:

	Theoretical for K <sub>2</sub> SO <sub>4</sub>	Residue examined.	
		(1) High results.	(2) Low results.
Potassium . . . . .	0.6694 g.	0.6699 g.	0.6664 g.
Sulphuric acid (SO <sub>4</sub> ) . . . . .	0.8220 g.	0.8175 g.	0.8162 g.
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	1.4914 g.	1.4874 g.	1.4826 g.

It will be seen that 1.4914 grams of the residue used, correspond to 14.81 cc. of solution, and should therefore contain 0.0100 gram iodine. The above analysis shows the difference between this amount of residue and the amounts of potassium and sulphuric acid (SO<sub>4</sub>) that it contains. The discrepancy between this difference and the amount of iodine that should be in the residue cannot be accounted for at present.

Although the results of this investigation have been negative in the main, nevertheless some information as to the behaviour of hydriodic acid in the presence of oxygen and

light has been ascertained. It has been shown that hydriodic acid in the presence of oxygen is slowly changed to something else, the colour of the solution due to the liberated iodine ultimately disappearing. This change is greatly accelerated by light. There is good reason to believe that the process of the change is one of oxidation, but all attempts to reduce this oxidation compound have failed, and the condition in which the iodine exists still remains unsolved.

In conclusion, my most hearty thanks are due to Professor Mackay for his valuable criticisms, and the kind interest he has taken in this investigation.

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