(3) It is shown that no appreciable error is introduced from this source, if a *dry* salt is fused in a current of hydrochloric acid which has been dried by phosphorus pentoxide.

(4) It is pointed out that in the case of hydrobromic acid diluted with twice its volume of nitrogen no similar effect is produced.

We are deeply indebted to the Carnegie Institution of Washington with whose generous aid this investigation has been completed, and also to the Cyrus M. Warren Fund for Research in Harvard University for indispensable platinum vessels.

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ON THE CHEMICAL ACTION OF ULTRA-VIOLET LIGHT.

BY W. H. ROSS.

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THE work herein described was undertaken with a view to making especially some quantitative measurements on the chemical action of light. Since in the majority of chemical changes the greatest effect is produced by ultra-violet light, it was thought advisable to work with a source of light rich in these rays. Such a source was obtained by causing an oscillatory spark to pass between aluminium terminals joined in the secondary circuit of a large induction coil used as a transformer. In the secondary circuit was also joined in parallel a large Leyden jar. Through the primary circuit was passed an alternating current of 110 volts having a strength of 3.4 amperes. To obtain a constant source of light proved a matter of considerable difficulty. However, by arranging an apparatus as thus described and having in the primary circuit an ammeter and resistance boxes, the resistance could be changed at will and the strength of the current thus kept constant. When a uniform current was in this way maintained, the amount of energy given out by the spark during intervals of ten minutes was practically constant. This was shown to be the case by the fact that the same amount of iodine was set free from equal volumes of a potassium iodide solution, when exposed to the light under exactly the same conditions for equal intervals of time. After every observation the aluminium terminals were sharpened, and then placed the same distance apart so that every exposure might be begun under the same conditions. The terminals used were large—3 mm. by 8 mm. cross-section—and were allowed to rest for the greater part of their length on iron plates placed 7 cm. apart. In this way the heat generated by the spark was rapidly conducted away. By placing the proper amount of ice in small dishes resting on the terminals, the temperature of a solution of 3 cc., placed in a cell directly underneath the spark, could be kept within a range of 1° during an exposure of ten minutes.

Aluminium terminals were used on account of the strong ultra-violet rays given out by a spark passing between them. The rate of decomposition produced by the light in the case of the iodides, when terminals of aluminium were used, was found to be at least twice as great as that resulting when terminals of any of the other common metals were used. Cadmium could not be used on account of its softness. An accurate comparison of the decompositions produced, when electrodes of different metals were used, was not made, since, on account of their difference in hardness, the experiments could not be carried out under comparable conditions.

DECOMPOSITION OF THE IODIDES.

The compounds first investigated were the iodides of the different metals in solution. The solution to be exposed to the light was placed in a shallow vessel directly underneath the spark. The amount of iodine set free was determined by titrating with a standard solution of sodium thiosulphate, using starch as indicator. When making exposures of ten minutes, the most convenient strength of the sodium thiosulphate was found to be 1/1000 normal. With a solution of this strength the amount of iodine set free could not be determined by titrating with the thiosulphate directly. By adding an excess of the thiosulphate solution, however, and then titrating with a 1/1000 normal solution of iodine, the amount of iodine set free could be accurately determined.

It was noticed when making titrations that the purest water obtainable, that used in this laboratory for making electrical conductivity measurements, had the power of decolorizing quite an appreciable amount of iodine. Thus, to 20 cc. of water, containing a few drops of starch solution, had to be added from

0.2 cc. to 0.4 cc. of a 1/1000 normal solution of iodine before any blue color appeared. With an iodide present a less amount of the iodine solution was required. Hence, before titrating any solution exposed to the light, a blank titration of a solution containing the same amount of iodide, was made in every case in order that the proper correction to be applied might be found.

When a solution of potassium iodide was exposed to the light in an open vessel, the amounts of iodine set free, on making exposures for equal intervals of time, varied greatly. When the distance of the solution from the spark was doubled, the rate of decomposition remained almost the same as before. The spark was then made to pass through an atmosphere of oxygen. This was done by placing the terminals in a large bell-jar filled with the gas. Under these conditions, the rate of decomposition was found to be very much increased. In replacing the oxygen with carbon dioxide, the amount of decomposition resulting in the same length of time was very small. It therefore became evident that the greater part of the decomposition first obtained was produced, not by the light only, but principally by the action of ozone and the oxides of nitrogen formed by the passage of the spark through air.

To determine the effect of the ultra-violet light only, the solution was placed in a small shallow dish provided with a quartz cover. The latter was sealed into a rim of hard rubber which was in turn surrounded by an elastic rubber band. This then could be slipped over the top of the dish so as to secure the complete exclusion of any gas. When the dish was now placed underneath the spark, the decomposition resulting represented the total effect of the waves of light given out by the spark. By subtracting from this the effect produced when a thick piece of glass plate was interposed between the spark and the solution, the effect of the ultra-violet light alone, or that part of it capable of being absorbed by the glass, was determined. When a photograph of the spectrum given by the spark was taken by means of a spectroscope, it was found that, when the glass plate used in the following experiments was interposed between the spark and the spectroscope, all wave-lengths were absorbed below λ 3260.

That the decomposition of the iodide, which took place when gases formed by the spark were excluded, was due to the action of the light alone was shown by varying the distance of the solution from the spark. It was now found that the amount of iodine set free varied inversely as the square of the distance, which one would expect if the decomposition is due entirely to the amount of light energy incident upon the solution. When making exposures, 3 cc. of the solution were taken in every case, while the time of exposure was ten minutes.

The effect produced on solutions of potassium iodide of different concentrations is shown in the following table:

Gram mol. KI per liter.	I set free measured in cc. of $N/1000$ solution.	Gram mol. KI per liter.	I set free measured in cc. of $N/1000$ solution.
3.0	3.58	0.05	1.50
2.0	3.35	0.02	1.15
1.0	3.00	0.01	1.00
0.5	2.68	0.005	0.80
0.2	2.15	0.002	0.50
0.1	1.85	0.001	0.40

Duplicate observations, which agreed with one another within 0.1 cc., were made in every case.

On varying the time of exposure, the amount of iodine set free was not at first exactly proportional to the time. This agrees with what might be expected for the color of the solution, or its power of absorption, changes after a short exposure. A tenth-normal solution was used in each case.

Time of exposure.	I set free in cc. of $N/1000$ solution.
10	1.85
20	3.30
30	4.90

When making these observations, the terminals were sharpened and placed the same distance apart every ten minutes.

When the glass plate already referred to was interposed between the spark and the solution, the amount of iodine set free was very small. Thus, in the case of a twice normal solution of potassium iodide, the amount set free was found to be equivalent to only 0.15 cc. of a 1/1000 normal solution of iodine, while in the case of a 1/10 normal solution no free iodine could be detected after an exposure of ten minutes. When working with the more concentrated solution, the amount of iodine set free by the action of the visible light was subtracted from the total amount set free to get the results given above.

The iodides of sodium, lithium, barium, calcium and zinc were next investigated, but all were found to give the same results as those given by potassium iodide.

Gram equivalents of iodide per liter.	Iodine set free in cc. of N/1000 solution.					
	KI.	NaI.	LiI.	BaI_2.	CaI_2.	ZnI_2.
2.0	3.35	3.40	3.35	3.45	3.37	3.40
0.5	2.68	2.60	2.65	2.70	2.73	2.70
0.1	1.85	1.80	1.85	1.75	1.80	1.85
0.01	1.00	1.00	1.05	1.00	1.03	1.00

These observations were made at a temperature of 18°. A variation, however, in the temperature of any of the solutions between 15° and 30° produced no appreciable change in the rate of decomposition.

REDUCTION OF FERRIC SALTS.

Solutions of the sulphate, nitrate and chloride were standardized by reducing with stannous chloride and then titrating with potassium permanganate in the presence of manganese sulphate and phosphoric acid. That the solutions thus standardized as regards the iron also contained equivalent amounts of acid, was shown by titrating a definite portion of each solution with a standard sodium hydroxide solution, using phenolphthalein as indicator.

When two Nessler tubes surrounded with white paper were filled with the standard sulphate and chloride solution, it was noticed that the first solution was slightly darker than the second, but on adding to it a few drops of acid it could be brought to the same color as the other when thus viewed by reflected light. When the tubes with the paper coverings removed were placed so as to view the solutions by transmitted light, the sulphate solution was now much lighter in color than the chloride solution. This shows that the two solutions have a different power of absorption for light. Hence, when acted upon by light of the same intensity, it was found, as might be expected for this reason alone, that the solutions were not reduced at the same rate.

As is well-known, the action of light on ferric salts is very much increased when there is present in solution some organic compound as cane-sugar, which of itself will not reduce the salts but does so under the influence of light. Hence, when working with these solutions a definite amount of sugar was always added.

The amount of salt reduced was determined by titrating with a standard 3/400 normal solution of potassium permanganate. When finding the effect of ultra-violet light on solutions of different strength, a 1/5 normal solution was first taken to which was added 10 grams of sugar per 50 cc. of solution. A 1/10 normal solution was then prepared by adding to a definite volume of the 1/5 normal solution an equal volume of water. Solutions of other dilution were prepared from the 1/5 normal solution in the same way.

With ferric chloride, sulphate and nitrate the following results were obtained on making exposures of ten minutes:

Gram-equivalents. of salt per liter.	Ferrous salt formed in cc. of $3N/400$ solution.		
	$FeCl_2$.	$FeSO_3$.	$Fe(NO_3)_2$.
0.20	2.50	2.45	0.55
0.10	2.25	1.70	0.50
0.05	1.93	1.05	0.48
0.02	1.27	0.50	..
0.01	0.85	0.40	..
0.005	0.70	..	..
0.002	0.60	..	..

The amount of sugar added has a considerable effect on the amount of reduction which takes place as is shown thus:

Percentage of sugar added.	$FeCl_2$ formed in cc. of $3N/400$ solution.
10	1.73
20	2.50
40	3.22

The amount of ferric salt reduced is approximately proportional to the time of exposure. A 1/5 normal solution of ferric chloride containing 10 grams of sugar per 50 cc. of solution gave results as follows:

Time of exposure.	$FeCl_2$ formed in cc. of $3N/400$ solution.
10 minutes	2.53
20 minutes	4.70
30 minutes	7.15

Varying the temperature of any ferric salt solution was found to have a slight effect on the rate of reduction.

REDUCTION OF CHLORATES AND BROMATES.

While solutions of the chlorates and bromates are quite stable in sunlight, they were found to be reduced to quite an extent when acted upon by that part of the ultra-violet spectrum capable of being absorbed by glass. The extent of the reduction was determined by titrating the amount of chloride or bromide formed by means of a 1/200 normal solution of silver nitrate. It was found that solutions of all chlorates of the same strength were reduced at the same rate, while the same thing was true of the bromates. The rate of reduction of the chlorates, however, differed from that of the bromates. Unlike the iodides or ferric salts, varying the strength of either the chlorate or bromate solutions from 1/2 to to 1/50 normal did not produce any appreciable difference in the amount of reduction which took place.

Gram-equivalents of $KClO_3$ [or $NaClO_8$, $Ba(ClO_3)_2$, etc.] per liter.	Chloride formed in cc. of N/200 solution.
0.50	0.80
0.10	0.80
0.02	0.80
0.01	0.78

In the case of the bromates the amount of salt reduced was less than in the case of the chlorates. Thus, when the strength of any standard bromate solution was varied from 1/2 to 1/100 normal, the amount of bromide formed in every case was equivalent to only 0.25 cc. of a 1/200 normal silver nitrate solution.

The amount of chlorate or bromate reduced was found to be exactly proportional to time of exposure.

Sugar added to solutions of the chlorates or bromates resulted in an increase in the amount of reduction which took place, but to a much less extent than in the case of the iron salts. Varying the strength of the solution now produced a change in the amount of reduction. A 1/2 normal solution of potassium chlorate containing 10 grams of sugar per 50 cc. of solution, when diluted so as to make a 1/20 normal solution, gave the same results, however, as one containing no sugar.

Gram mol. of $KClO_8$ per liter.	Chloride formed in cc. of N/200 solution.
0.5	1.50
0.2	1.15
0.1	0.90
0.05	0.80
0.01	0.80

When sugar was added to the bromate solutions, a greater amount of reduction took place than in the case of the chlorates.

Gram mol. of bromate per liter.	Bromide formed in cc. of N/200 solution from $KBrO_3$.	$NaBrO_3$.	$Ba(BrO_3)_2$.
0.5	1.75	1.73	1.75
0.2	1.55	1.50	1.55
0.1	1.40	1.42	1.37
0.05	1.20	1.20	1.25

Before making a titration to determine the amount of change produced in any particular solution, a blank titration was first made in every case.

I wish to express my thanks to Professors Jones and Wood at whose suggestion this work was undertaken.

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A GAS GENERATOR FOR HYDROGEN SULPHIDE, HYDROGEN AND OTHER GASES.

BY ALLEN P. FORD.

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THE principle of the generator shown in the accompanying sketch is by no means new. The general form of the present apparatus was shown and described[1] by H. G. Schanche. An improved form was described[2] by Augustus E. Knorr, the improvement consisting essentially of a siphon tube which allowed automatic escape of the exhausted acid.

A generator was made in our laboratory after the plan of this improved one, which worked well, but it was found that the water in the wash-bottle would suck back into the calcium chloride jar over night, owing to the absorption of the gas and the consequent creation of a partial vacuum. This, together with the fact that it sometimes did not start up readily after lying idle some time, owing to the accumulation of sediment and crystallized salts, gave considerable annoyance, and the result of the experience and consequent experimenting is the form of apparatus shown herewith.

It needs no detailed description as the cut is self-explanatory. The apparatus is self-sustaining, all being carried on one base with the exception of the small wash-bottle. The automatic overflow for the spent acid is out of the way, a small hole in the

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[1] This Journal, **16**, 868 (1894).

[2] Ibid. **19**, 818 (1897).