XXV.—*Decomposition of Potassic Chlorate by Heat in the presence of Manganic Peroxide.*

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THE familiar process of preparing oxygen by heating a mixture of potassic chlorate and manganic peroxide, first described by Döbereiner in 1832 (*Annalen*, **1**, 236—237), has been investigated by many chemists in the endeavour to trace the cause of the very ready decomposition of the chlorate; the matter, however, seems to be still rather obscure, and the experiments described in this note were undertaken in the hope of farther elucidating the subject.

Many years ago it struck me that the physical condition of the manganic peroxide was changed by heating with the chlorate, and I made a few experiments on the subject, but without any satisfactory result.

During the last three months a series of experiments has been made with various kinds of peroxide of manganese, and there is no doubt about the change of the peroxide.

The temperature employed has usually been that of boiling mercury, and the experiments have been carried out in the simplest way. A test-tube was weighed and about a gram of powdered potassic chlorate (which had been once recrystallised from water, powdered, and dried in a water-oven) and about 1/10th of its weight of manganic peroxide were introduced. The test-tube, attached by a bent tube and corks to a U-tube containing a solution of potassic iodide, was then placed into a wider test-tube, containing a small quantity of mercury, and the latter heated until the vapour of the mercury rose some distance above the mixture in the interior tube.

Potassic chlorate undergoes no perceptible decomposition at the temperature of boiling mercury; the powder, however, cakes together, and when the experiment is observed under the microscope there is an appearance of incipient fusion. In one experiment (I) (see Table, p. 193) 1·7107 grams of potassic chlorate was heated in mercury vapour for an hour and lost 0·0018 gram, or 0·105 per cent. In another case (XVII), 1·4402 gram of the chlorate was heated for 10 hours and the loss was 0·0024, or 0·167 per cent. This experiment was done under the microscope, and there were signs of fusion in 15 minutes after the heating commenced. The loss in weight was probably due to the presence of a small quantity of water.

The oxide of manganese used was obtained from various sources. Some, called "crystalline," obtained from Messrs. Hopkin and Williams, was in fragments of a crystalline structure; this was broken up in a mortar and levigated, the very fine particles being rejected. The rest was dried and sifted, the portion which remained between sieves with apertures of 0·19 and 0·16 mm. was kept and called "granular oxide;" it contains a small quantity of iron.

Some manganic peroxide was prepared by adding a solution of bleaching powder to a solution of manganous chloride, the precipitate was collected and washed, and afterwards boiled in acetic acid to remove any calcic carbonate present. It was then washed, dried, and heated for some time in a test-tube surrounded with mercury vapour. The compound was found from its loss on ignition to be Mn_5O_9.

A specimen of crystalline pyrolusite was used in some experiments. This was powdered and levigated, and the coarser portions employed.

I am indebted to Mr. V. H. Veley for two specimens of manganic peroxide, one of which was precipitated by the action of chlorine on pure manganous acetate (Trans., 1880, **37**, 581). Mr. Veley attributes to this compound the formula $Mn_6O_{11} + xOH_2$. When dried, first in the water-oven and afterwards in the vapour of boiling mercury, it lost 7·182 per cent. The other specimen was a piece of finely crystallised pyrolusite from Windsor, Nova Scotia; it contains a trace of iron.

The first experiment (II) was made with 1·0276 grams of potassic chlorate mixed with 0·1015 gram of "granular peroxide." The test-tube was heated in a beaker of mercury. At 13° below the temperature at which the mercury boiled, gas came off slowly, but at the boiling point the evolution was rapid. The solution of potassic iodide was coloured, and on titration with sodic thiosulphate it was found that the amount of chlorine which had been evolved was 0·0375 per cent. of the quantity of chlorate employed. The loss of weight of the test-tube and contents was 0·3975 gram, or 38·682 per cent. of the chlorate used. Taking 39, 35·37 and 15·96 as the atomic weights of potassium, chlorine, and oxygen respectively, the percentage of oxygen in potassic chlorate is 39·166. The residue in the test-tube was extracted with water and filtered through a weighed filter, the manganic peroxide was now in a very fine state of division and weighed 0·1007 gram, or 99·211 per cent. of the quantity taken.

In the next experiment (III), the mixture was heated in the vapour of mercury; the mixture suddenly softened and swelled up, and gas was evolved so rapidly that some of the potassic iodide solution was projected from the U-tube, and white fumes were seen. Doubtless some of the mixture was carried over mechanically. The loss of weight was 39·145 per cent., the quantity of chlorine 0·0283 per cent., and the manganic peroxide recovered 98·5 per cent.

When the mixture of potassic chlorate and granular peroxide was heated by a gas flame, the evolution of oxygen was more violent, and some of the mixture was carried over by the gas. In one experiment (V), the loss was 39·380 per cent., and the peroxide recovered was only 97·294 per cent. In this case more chlorine was evolved, being 0·047 per cent. of the chlorate taken.

With the specimens of pyrolusite, the action was not so rapid, and less chlorine was evolved (VI, VII, and VIII).

With precipitated peroxide, the action is much more violent, the action being completed in about five minutes. There was usually a loss of solid matter from the tube, and more chlorine was evolved (IX, X, and XI).

It has been stated that the manganic peroxide loses its power of decomposing potassic chlorate, and therefore cannot be used over and over again (E. O. Brown, quoted by Baudrimont,* *J. Chem. Soc.*, 1871, **24**, 1151). To test this, a quantity of granular peroxide rather finer than that used in the previous experiments was heated in a test-tube with potassic chlorate over a gas flame, the mass washed with water, and the insoluble residue dried. This operation was repeated nine times, and the washed and dried oxide was heated with potassic chlorate in the vapour of mercury. In this case (XII), the quantity of peroxide was only 6·8 per cent. of the amount of chlorate, and yet the action was

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* This paper appeared in the *Journal de Pharmacie et de Chimie* [4], **14**, 84—94, 161—177. (In the *Journal of the Chemical Society* it is quoted from *J. pr. Chem.*, which is obviously an error.) In the original, it is not stated that Brown had asserted that the oxide was exhausted by use, and in the same vol. of the *Journ. Pharm.*, p. 22, there is a report on the preparation of oxygen by Coulier, Limousin, J. Regnauld, Jungfleisch, and Baudrimont, in which it is stated on p. 77 that the oxide does not lose its activity by previous use. I did not see these papers until the work was nearly completed; I would strongly recommend them to the attention of all chemists working on this subject.

very violent, and complete in two minutes. The loss was 39·121 per cent. and the amount of chlorine 0·045 per cent. The peroxide was entirely changed in appearance, and was brown instead of black. This shows that the peroxide cannot be exhausted by use, and the change of character seems to indicate that the peroxide had entered into chemical action and had been reproduced.

It will be noticed that in all these experiments an appreciable quantity of chlorine is evolved together with the oxygen. This evolution of chlorine is well known and has been frequently described. The questions arise, what is the source of this chlorine? and is its evolution a necessary accompaniment of the action of the manganic peroxide on the potassic chlorate?

The specimen of precipitated manganic peroxide which gave the largest quantity of chlorine was prepared from manganous chloride by the action of solution of bleaching powder, and when it was first prepared it contained a small quantity of chlorine. After having been heated in the vapour of mercury, however, this chlorine was eliminated. If all the chlorine evolved in Experiment IX had come from the manganic peroxide, the latter would have contained nearly $2\frac{1}{2}$ per cent. of it.

When sodic chloride is heated in a test-tube with manganic peroxide over a gas flame, a very perceptible quantity of chlorine is evolved. A small quantity is also liberated when the mixture is heated to the boiling point of mercury, so perhaps it is more a matter of surprise that so little chlorine is present in the oxygen obtained from potassic chlorate and peroxide of manganese than that any should be produced.

To see if the addition of a body that would prevent the evolution of chlorine would affect the liberation of the oxygen, two experiments were made, in one of which (XIII) about half a per cent. of sodic carbonate was added to the mixture. At the boiling point of mercury, less than 6 per cent. of oxygen was evolved in half an hour. On heating over a gas flame, the action was not rapid and the fused mass appeared greenish; and on cooling, a small quantity of permanganate was observed. In the other experiment (XIV), about the same quantity of potassic carbonate was used; about 8 per cent. of oxygen was evolved at the boiling point of mercury, and more than the theoretical loss was observed after heating with a gas flame; this was probably due to loss when the test-tube melted.

As a considerable quantity of the manganic peroxide did not seem to be broken up when heated with the chlorate, some experiments were made to see if a much smaller quantity of the peroxide was capable of effecting the complete decomposition of the salt. In

Experiment XV less than 1 per cent. of the peroxide was used, and although the gas was evolved very slowly (the heating being continued for 5 hours and 20 minutes), yet ultimately almost the theoretical quantity of oxygen was liberated.

A still smaller quantity of peroxide also affects the chlorate, but much more slowly; in Experiment XVI only 0·1 per cent. was used, and after 22 hours 40 minutes 6·289 per cent. of oxygen had been evolved. An accident prevented the experiment being carried farther.

In those experiments in which the quantity of peroxide is very small, the white [chlorate covers the granules and only a few black specks are visible. When such a mixture is heated, it is very curious to observe the formation and growth of grey spots starting from the granules, these spots increasing until the whole mass is uniformly grey. It seemed to be interesting to study the course of this change, and for this purpose a small quantity of potassic chlorate was placed in a test-tube with a single granule of the peroxide. The test-tube was inserted in a wider tube with some asbestos at the bottom, and the bulb of a thermometer was placed close to the bottom of the inner test-tube. A microscope with a 4-inch objective was arranged horizontally so that the granule of peroxide could be watched, the light from a gas flame being condensed on the object by a lens. The bottom of the outer tube was heated by a gas flame; and when the temperature reached 350° or thereabouts there were signs of fusion around the granule of peroxide, and the black mass appeared to glisten as if wetted or attacked; as it was not possible to maintain the temperature very constant, it was allowed to rise until the chlorate was all fused, when the peroxide was found to be broken up into minute fragments, each of which was a nucleus from which gas bubbles rose. On cooling, the fused mass had a distinct pink tinge as if permanganate had been formed; the colour could not have been due to potassic ferrate, for the tint produced by this compound is quite different.

In another experiment (XVII), to which reference has previously been made, 1·4402 grams of chlorate were heated for 10 hours in the vapour of mercury before the microscope; the loss was only 0·167 per cent. A fragment of granular peroxide weighing 0·0002 gram or 0·014 per cent. was then introduced and the heating recommenced. Minute particles soon became detached from the fragment, and the chlorate fused and flowed down in a stream between the glass and the rest of the salt, carrying the particles with it. The tube was allowed to cool and examined, and the mass was found to present the appearance so often observed; the grey stain having spread for some distance from the granule. The heating was continued for 4½ hours, and some of the chlorate fused. The loss was 0·847 per cent. On cooling the mass was pink.

In Experiment XVIII, a brilliant crystal of pyrolusite from Windsor, Nova Scotia, was placed in a test-tube containing powdered potassic chlorate. This was heated in the vapour of mercury before the microscope. The salt soon fused in contact with the crystal, and an action was seen to take place on the surface of the latter. The crystal afterwards broke up into fine needle-shaped fragments, and in 55 minutes the whole of the salt was fused. After cooling, the mass was pink.

The evolution of chlorine during the action of manganic peroxide on potassic chlorate, and also the pink colour which is seen when the manganese compound is used in small quantities, seem to indicate that the formation of a permanganate may have something to do with the rapid evolution of oxygen; this has often been suspected by chemists. Some experiments were instituted to endeavour to prove this presumption.

An experiment (XIX) was made to determine the temperature at which the potassic permanganate is decomposed. Some crystals of air-dried permanganate were powdered and heated in mercury. Gas began to come off at 250°, and the evolution was rapid at 260°; at 275° the decomposition ceased. The mass in the test-tube had not fused, but it was almost black, and when water was added a deep-green solution was produced. The loss on heating was 11·176 per cent. In two other experiments the loss was 12·14 and 12·136 per cent. respectively.

It is usually stated in text-books that potassic permanganate is decomposed by heat into potassic manganate, manganic peroxide, and oxygen, thus:—$K_2Mn_2O_8 = K_2MnO_4 + MnO_2 + O_2$. Taking the atomic weight of manganese at 55, this would involve a loss of 10·126 per cent. of oxygen. The loss of 11·176 per cent. more nearly agrees with the equation $10K_2Mn_2O_8 = 10K_2MnO_4 + 2Mn_5O_9 + 11O_2$. The quantity required by this change is 11·139 per cent. The loss 12·14 agrees nearly with the equation $5K_2Mn_2O_8 = 5K_2MnO_4 + Mn_5O_8 + 6O_2$, which requires 12·15 per cent. Too much reliance must not be placed on these results, as no endeavour was made to obtain pure permanganate; the specimen used was a well-crystallised sample of the commercial salt.

Several experiments were made to try the effect of the presence of different quantities of potassic permanganate on the decomposition of potassic chlorate in contact with manganic peroxide. In XX, XXI, XXII, and XXIII the percentage of permanganate to the chlorate was 0·151, 0·201, 0·449, and 0·491 respectively, and it will be seen that as the permanganate increased the quantity of chlorine evolved diminished, none whatever being liberated in the last case. In the first, where the very small percentage of permanganate was used, the quantity of chlorine is notably less than in other cases where chlorate and the granular peroxide were heated together (II, III, IV, and V). The presence of the permanganate, however, very perceptibly diminished the rate of decomposition of the chlorate.

When the percentage of permanganate was raised to 2·3 (XXIV), the time was still further prolonged, so that in 1 hour 50 minutes little more than two-thirds of the chlorate was decomposed. The residue, after heating, contained manganate.

A mixture of nearly equal quantities of potassic chlorate and potassic permanganate was heated in mercury (XXV), the permanganate underwent its usual decomposition, there being 11·468 per cent. of its weight of gas evolved below 275°. On again heating in mercury, gas came off freely at 350°, and quickly at 356°. The mass was caked but not fused; on farther heating in the vapour of mercury for 35 minutes, very little more gas was evolved. Almost the whole of the oxygen of the chlorate was liberated. On adding water to the residue, the solution was green.

Another similar mixture (XXVI) was heated in mercury vapour. Gas at first came off rapidly and then diminished in quantity; it subsequently came off very rapidly, and some solid was carried over mechanically; the decomposition was completed in 10 minutes. The residue was not fused, and was found to contain manganate. The loss was 0·2425 gram, whereas the quantity of oxygen that might be expected from the permanganate and chlorate is 0·2404; the excess of loss was probably due to the solid that was carried over.

These experiments would seem to indicate that potassic manganate will not assist the decomposition of the chlorate, and that when the mixture of chlorate and permanganate is heated, the former is decomposed by the oxide of manganese liberated during the decomposition of the latter.

When potassic chlorate is fused with a very small quantity of manganic peroxide, a pink colour is observed in the mass on cooling, as before stated. When this pink mass is fused over a flame, oxygen is evolved, but the colour persists until nearly all the chlorate is decomposed; it then becomes greenish, and when further heated the fused residue of chloride has a brownish appearance. If the pink colour is due to permanganate, as seems most probable, it would appear to indicate that the permanganate is being continually reproduced as rapidly as it is decomposed by the heat, for the above Experiments XXI to XXVI prove that permanganate is decomposed in the presence of potassic chlorate. When the peroxide is used in large quantities, the pink colour is masked by the black oxide, although it can hardly be doubted that it is really formed. This observation seems to supply the key to the question.

At first sight, it appears impossible that a compound can be formed at a temperature at which it is decomposed, but we have a somewhat analogous case with ammonia, which is decomposed by electric sparks, and yet when sparks are passed through a mixture of hydrogen and nitrogen, small quantities of ammonia are formed.

It has been stated by H. N. Warren (*Chem. News*, **58**, 247) that when potassic chlorate and manganic peroxide are heated in an iron tube and the residue extracted with water, the solution is alkaline. I have often tested the solutions obtained from the residues after heating in test-tubes, but have never been able to recognise the faintest trace of alkalinity; the same result was found with the residue after heating in a platinum crucible; but if the residue had been strongly ignited, the solution was alkaline.

It has been shown by Eccles (*J. Chem. Soc.*, **29**, 857) that potassic perchlorate is not formed when potassic chlorate and manganic peroxide are heated together; and I have found that when perchlorate is heated with the peroxide to the temperature of boiling mercury it does not lose oxygen. To the residue some potassic chlorate was added and the mixture again heated, when nearly the theoretical quantity of the oxygen from the chlorate alone was evolved. This observation entirely confirms that of Eccles.

If the manganic peroxide undergoes a chemical change, first entering into combination and then being reproduced, it seemed to be of interest to try the effect of one of the other oxides of manganese, for if this acted similarly it might be expected that after the action it would be found to have been changed into the peroxide.

Some precipitated manganic peroxide was heated in a platinum crucible to dull redness and weighed. It was then ignited for 45 minutes, by which it is said to be converted into Mn_3O_4. Some of it was mixed with potassic chlorate and heated in the vapour of mercury (XXVII). The mass fused and the chlorate was entirely decomposed although very slowly; very little chlorine was evolved. The insoluble residue was a little heavier than the oxide taken, amounting to 100·929 per cent.

Another quantity of the ignited oxide was heated in a muffle for two hours, when it lost 1·304 per cent. Some of this oxide was mixed with the chlorate and heated for three hours in the vapour of mercury (XXVIII). No chlorine was evolved, but the chlorate evolved nearly the whole of its oxygen. The oxide recovered was 98·071 per cent. of that used. If the oxide had been entirely transformed into MnO_2 about 114 per cent. should have been collected. In a note to the Report of Messrs. Coulier, &c., above quoted, it is said, on p. 27, that

Mn_3O_4 is no less active than MnO_2. Baudrimont (*loc. cit.*, p. 163) states that Mn_3O_4 acts more feebly than MnO_2.

It may be the fact that only a very small portion of the manganic peroxide is converted into another compound, the remaining portions merely acting as nuclei for the liberation of gas. It is noticeable that in the test-tubes in which the mixture of potassic chlorate and the peroxide is heated, a deposit of very fine powder is always observed on the glass which has been in contact with the mixture. This adheres firmly and is not removed by merely washing with water. Probably this represents some of the peroxide which has been reproduced.

Two experiments were made with a mixture of chlorate and platinum-black (XXIX and XXX), to see if a substance which might be expected to be chemically inert would assist in the decomposition of the chlorate, the particles acting merely as nuclei; in the first, 19·345 per cent. of gas was evolved in one hour, and in the other the mixture was heated for $9\frac{1}{2}$ hours with two interruptions; when weighings were made, 28·111 per cent. of oxygen was evolved, so that the chlorate was far from being entirely decomposed. The most remarkable result was the evolution of about 0·02 per cent. of chlorine, so possibly a platinate or platinite was formed and immediately decomposed; the chlorine, however, may be due to insufficient washing of the platinum-black, which was made by reducing platinic chloride by sodic formate.

From the foregoing experiments, the mechanism of the action of manganic peroxide on the potassic chlorate, under the influence of heat, seems to be something of the following kind:—Firstly, the peroxide acts on the chlorate forming permanganate, chlorine, and oxygen. $2MnO_2 + 2KClO_3 = K_2Mn_2O_8 + Cl_2 + O_2$. Chlorine is certainly evolved as soon as the action commences. The permanganate then undergoes decomposition by the heat, producing manganate, an oxide of manganese and oxygen; for simplicity we may use the ordinary equation $K_2Mn_2O_8 = K_2MnO_4 + MnO_2 + O_2$. The third stage is not quite so clear; it is very improbable that the manganate is transformed into permanganate by the oxygen from the chlorate, for in Experiments XXIV and XXVI, in which permanganate and chlorate were heated together, manganate remained in the residue. It is more likely that the manganate is acted on by more chlorine produced by the action of the peroxide on fresh chlorate, thus, $K_2MnO_4 + Cl_2 = 2KCl + MnO_2 + O_2$. I have found that when chlorine is passed into the residue obtained by heating potassic permanganate, the residue being heated in the vapour of mercury, chlorine is absorbed and oxygen evolved. In this case, however, the action proceeds further, for not only is the potassium transformed into chloride but much of the manganese is also converted into chloride.

	Potassic chlorate used.	Manganic peroxide used.		Other bodies used.		Loss.		Chlorine, per cent. on potassic chlorate.	Manganic peroxide recovered. Per cent. on that used.	Source of heat.	Time of heating.	
		Grams.	Per cent. on chlorate.	Grams.	Per cent. on chlorate.	Grams.	Per cent. on chlorate.					
	grams.										h. m.	
I.	1·7107	—	—	—	—	0·0018	0·105	—	—	mercury vapour	1 0	Salt caked in test-tube.
II.	1·0276	granular 0·1015	9·877	—	—	0·3975	38·682	0·0375	99·211	mercury	—	Gas came off slowly 13° below boiling point of mercury. When mercury boiled, gas came off quickly.
III.	2·3714	granular 0·2467	10·403	—	—	0·9284	39·145	0·0283	98·500	mercury vapour	—	Gas came off rapidly, mass softened and swelled up; some of the potassic iodide projected from U-tube.
IV.	1·0977	granular 0·1107	10·085	—	—	0·4220	38·444	0·044	—	mercury vapour	0 30	Mass grey, and swelled up in 3 min. Gas came off regularly. Action complete in 15 min.
V.	1·0203	granular 0·1035	10·144	—	—	0·4018	39·380	0·047	97·294	gas flame	—	Gas came off quickly. Some white deposit found in delivery tube.
VI.	1·0041	crystalline 0·1013	10·088	—	—	0·3887	38·711	0·0095	96·742	mercury vapour	1 0	Gas came off rather slowly. Mass fused up.
VII.	1·0674	crystalline 0·1015	9·509	—	—	0·4138	38·767	0·0134	—	mercury vapour	—	

	Potassic chlorate used.	Manganic peroxide used.		Other bodies used.		Loss.		Chlorine, per cent. on potassic chlorate.	Manganic peroxide recovered. Per cent. on that used.	Source of heat.	Time of heating.	
		Grams.	Per cent. on chlorate.	Grams.	Per cent. on chlorate.	Grams.	Per cent. on chlorate.					
	grams.										h. m.	
VIII.	1·0035	crystalline Nova Scotian 0·0993	9·895	—	—	0·3913	38·993	0·028	97·482	mercury vapour	1 45	Gas came off regularly. Almost stopped in 8 min. Plug of solid had been forced up tube. Mercury boiled more rapidly, and more gas came off.
IX.	1·0367	precipitated 0·1105	10·659	—	—	0·4068	99·240	0·258	—	mercury vapour	0 10	Violent action which ceased in 5 min. Some MnO_2 carried over with the gas.
X.	0·9928	Veley's precipitated 0·0968	9·750	—	—	0·3922	39·504	0·115	—	mercury vapour	—	Gas came off violently, plug of solid blown up tube, and became incandescent. Finished in 4 min.
XI.	0·9874	Veley's precipitated 0·0922	9·338	—	—	0·3911	39·609	0·087	96·746	mercury	—	Bubbles passed during heating. At 320° U-tube contained oxygen. Evolution violent at 340°, and complete in 15 sec. Mercury boiled at 353°. No more gas in 10 min.

XII.	0·8535	granular, which had been used 9 times 0·0584	6·842	—	—	0·3339	39·121	0·045	94·007	mercury vapour	0 20	Gas came off very quickly, finished in 2 min. White fumes in U-tube. MnO_2 very finely divided.
XIII.	1·1126	granular 0·1027	9·230	sodic carbonate 0·0065	0·584	0·0643	5·779	0	—	mercury vapour	0 30	Gas came off very slowly, but mass fused.
						0·4329	38·908	0	100·681	gas flame	—	Action not rapid. During fusion, the liquid appeared greenish. Small trace of permanganate when cold. MnO_2 not much broken up.
XIV.	1·0013	granular 0·1038	10·366	potassic carbonate. 0·0060	0·599	0·0821	8·199	0	—	mercury vapour	0 30	Mass grey in 2 min. Swelled up in 4 min. Liquid in 6 min. Gas came off slowly.
						0·4034	40·287	0	99·036	gas flame	—	Action rapid. Part of mass became red hot. Test-tube was attacked. MnO_2 not much broken up.
XV.	1·2438	granular 0·0116	0·932	—	—	0·4752	38·205	0·0069	81·896	mercury vapour	5 20	Black spots appeared in 5 min. The mass became grey all over and fused in 6 min., and effervesced; gas came off slowly.
XVI.	1·1131	granular 0·0011	0·099	—	—	0·0700	6·289	0	—	mercury vapour	22 40	Grey spots grew in the chlorate. After 15 min. gas bubbles were formed, and the mass seemed semi-fused. In 40 min. the mixture was fused.

	Potassic chlorate used.	Manganic peroxide used.		Other bodies used.		Loss.		Chlorine, per cent. on potassic chlorate.	Manganic peroxide recovered. Per cent. on that used.	Source of heat.	Time of heating.	
		Grams.	Per cent. on chlorate.	Grams of potassic permanganate.	Per cent. on chlorate.	Grams.	Per cent. on chlorate.					
XVII.	grams. 1·4402	—	—	—	—	0·0024	0·167	—	—	mercury vapour	h. m. 10 0	Before microscope. In 15 min. there were signs of fusion, and the mass sintered together.
		granular 0·0002	0·014	—	—	0·0122	0·847	—	—	mercury vapour	4 30	Particles of the peroxide became detached and the chlorate fused in contact with it, the particles running over the chlorate. Trace of permanganate formed.
XVIII.	0·5340	pyrolusite from Nova Scotia 0·0018	0·337	—	—	0·0052	0·973	—	—	mercury vapour	0 55	Salt soon began to fuze in contact with the crystal of pyrolusite. Crystal afterwards broke up, and gas was evolved. All the salt fused in 55 min. Mass had pink tinge when cold.
XIX.	—	—	—	0·6013	—	0·0672	11·176	—	—	mercury	—	Gas began to come off at 250°. Rapid evolution at 260°. Evolution ceased at 275°. Mass not fused;

												almost black. Treated with water gave a green solution.
XX.	1·1946	granular 0·1182	9·894	0·0018	0·151	0·4653	38·950	0·016	98·985	mercury vapour	0 15	Gas came off regularly, but not so rapidly as in the absence of permanganate. Mass fused up.
XXI.	0·9958	granular 0·1118	11·227	0·0020	0·201	0·3796	38·120	0·014	—	mercury vapour	0 25	In 2⅓ min. gas came off quickly and mass softened. Fused and effervesced in 3 min. Violent evolution in 6½ min. Residue did not give green solution on extracting with water.
XXII.	1·1341	granular 0·1043	9·196	0·0051	0·449	0·4378	38·603	0·0041	—	gas flame	—	Heated quickly. Some of the powder carried over mechanically.
XXIII.	1·0995	granular 0·1025	9·322	0·0054	0·491	0·4262	38·763	0	98·829	mercury vapour	2 0	Gas came off very slowly.
XXIV.	1·0033	granular 0·1022	10·186	0·0231	2·302	0·2924	29·143	0	—	mercury vapour	1 50	Mixture swelled up in 3 min.; liquid in 4 min. Gas came off very slowly. Residue contained manganate.
XXV.	0·5486	—	—	0·5197	94·732	0·0596	on permanganate 11·468	—	—	mercury vapour	—	Gas came off at 250°, freely at 260°. Stopped at 275°. Powder not fused.
						0·2055	on chlorate 37·459	0	—	—	—	At 345° gas came off freely, at 350° quickly. Mass caked, but not fused.
						0·2079	37·896	—	—	mercury vapour	0 35	Very little gas came off.

	Potassic chlorate used.	Manganic peroxide used.		Other bodies used.		Loss.		Chlorine, per cent. on potassic chlorate.	Manganic peroxide recovered. Per cent. on that used.	Insol. residue recovered. Per cent. on Mn_3O_4 used.	Source of heat.	Time of heating.	
		Grams.	Per cent. on chlorate.	Grams.	Per cent. on chlorate.	Grams.	Per cent. on chlorate.						
	grams.											h. m.	
XXVI.	0·4867	—	—	potassic permanganate 0·4629	95·110	0·2425	—	0	—	—	mercury vapour	0 10	Gas came off at first rapidly, then slacked, then very rapidly. Some solid carried over. Mass not fused. Contained manganate.
XXVII.	1·0708	—	—	Mn_3O_4 0·1076	10·048	0·4113	38·410	very little	—	100·929	mercury vapour	—	Gas came off very slowly. Mass fused.
XXVIII.	1·1438	—	—	Mn_3O_4 0·1037	9·070	0·4361	38·144	0	—	98·071	mercury vapour	3 0	Mass blackened, fused, and effervesced.
XXIX.	1·2125	—	—	platinum black 0·1005	8·289	0·2346	19·345	0·023	—	—	mercury vapour	1 0	Mass blackened, fused, and effervesced.
XXX.	1·1892	—	—	platinum black 0·1148	9·654	0·2943	24·748	·020	—	—	mercury vapour	3 15	
						0·3088	25·967		—	—	—	2 0	
						0·3343	28·111		—	—	—	4 15	

If this took place in the preparation of oxygen, the solution obtained by extracting the residue with water would contain manganese, which is not the case. Moreover, manganous chloride cannot exist at a high temperature in the presence of potassic chlorate, for it is immediately transformed into an oxide with evolution of chlorine. If the chlorine, which might be produced by the action of the peroxide directly on the chlorate, is thus absorbed by the manganate, it fully explains the very small quantity of chlorine that is evolved, for in the case in which the largest proportion was found (IX), when precipitated peroxide was used, it corresponds to only 6 per cent. of the peroxide present, and as the action in this case was of a very violent character it is not improbable that much of the chlorine was due to the subsequent action of the peroxide on the potassic chloride. In the experiment in which granular oxide was used and the mixture heated over a gas flame (V), the quantity of chlorine corresponds to little more than 1 per cent. of the peroxide.

The table (p. 191, *et seq.*) contains the details of the experiments referred to in the paper; they are not, however, given in the order in which they were actually made.