

CVIII.—*The Decomposition of Chlorates. Part V.  
Potassium Chlorate in presence of Oxides of Man-  
ganese, and the Theory of Perchlorate Formation.*

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THE main object of the work now published was to ascertain the actual mechanism of the ready evolution of oxygen from a heated mixture of potassium chlorate and oxides of manganese, and to test the probability of the numerous chemical theories of this action which have been advanced from time to time. The "mechanical" hypothesis was dealt with in Part IV (Trans., 1901, 79, 939).

The present paper deals with the qualitative action of oxides of manganese rather than with the quantitative relations of any particular oxide.

It seems doubtful whether anyone has obtained a substance having the exact composition required by the formula  $MnO_2$ , but all the oxides of manganese between  $MnO$  and  $MnO_2$  facilitate the decomposition of potassium chlorate. It is stated that an intermediate oxide finally results whichever oxide is used.

The expression "manganese peroxide" will be employed in the sense of  $MnO$ ,  $nMnO_2$ ,  $mH_2O$ , where  $n$  is large and  $m$  small, as water is obstinately retained, even when the oxide is heated until a little oxygen has been given off. The effect of adding various substances to potassium chlorate has been dealt with in numerous papers, of which it will be necessary to quote those of Baudrimont (*J. Pharm. Chim.*, 1871, [iv], 14, 81, 161), Jungfleisch (*ibid.*, 1871, [iv], 14, 130), H. Schulze (*J. pr. Chem.*, 1880, [ii], 21, 426), Hodgkinson and Lowndes (*Chem. News*, 1888, 58, 309; 1889, 59, 63), Veley (*Phil. Trans.*, 1888 A, 271), Fowler and Grant (*Trans.*, 1890, 57, 272), and McLeod (*Trans.*, 1889, 55, 184; 1894, 65, 202; 1896, 69, 1015).

Brunck (*Ber.*, 1893, 26, 1790, and *Zeit. anorg. Chem.*, 1895, 10, 222) maintained that the active oxidising substance present in the gas evolved from potassium chlorate and manganese peroxide was a peculiar form of ozone resembling chlorine in some of its properties, but McLeod, in his two later papers, appears to have proved conclusively that it is actually chlorine.

*The Nature of the Cycle of Changes.*—The possibility of "mechanical" facilitation has been dealt with in Part IV (*loc. cit.*), and there are, in addition, several reasons for believing the effect of manganese peroxide to be due to chemical action, for example, under the microscope, the particles are seen to be attacked and broken up (McLeod, 1889), and an evolution of oxygen can be produced without fusing the chlorate (Baudrimont, Veley).

Any chemical explanation must be of the nature of a cycle of changes, and with only three elements in addition to manganese all possibilities would seem to be included in one or other of the following three classes:

(1) Cycles in which the formation of a compound containing manganese and *potassium* is included.

(2) Cycles in which the formation of a compound containing manganese and *chlorine* is included.

(3) Cycles confined to alternate oxidation and deoxidation.

As an example of class (1), we may take the theory usually given in text-books (McLeod), it being suggested that permanganate, chlorine, and oxygen are first formed,  $2KClO_3 + 2MnO_2 = 2KMnO_4 + Cl_2 + O_2$ , the permanganate then breaks up approximately in accordance with the equation  $2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$ , and nearly all the chlorine reacts with the manganate,  $K_2MnO_4 + Cl_2 = 2KCl + MnO_2 + O_2$ .

The experiments of McLeod and others tend to indicate that a trace of permanganate is formed, and that all these reactions *may* occur during a decomposition, but the author is not aware of anyone having attempted to show that these changes *do* actually occur to any considerable extent. It is easy to devise similar cycles in which the first reaction produces manganate or manganite instead of permanganate.

If the breaking up of the chlorate be due to a cycle of this class, the whole of the chlorine must be progressively liberated and reabsorbed with the exception of a trace.

To illustrate class (2), suppose the very unstable manganous chlorate were formed, this would immediately break up, yielding much free chlorine (Wächter, *J. pr. Chem.*, 1843, 30, 325); any resulting manganous chloride would at once be violently converted into peroxide by the action of the heated chlorate (H. Schulze; McLeod, 1889). Here, again, the whole of the chlorine would be liberated, but reabsorption might be brought about by the potassium oxide first formed. It seems unlikely that there should be any marked formation of manganous chlorate, for it has been repeatedly shown that neither magnesia nor zinc oxide produces any appreciable acceleration in the reaction, although both are far more basic than the oxides of manganese.

It will be seen that cycles belonging to class (3) are the only ones which do not involve the setting free of the whole of the chlorine contained in the chlorate, coupled with an almost complete reabsorption.

TABLE I.—*Effects of Variation of Pressure.*

Chlorate.	Under reduced pressure.			Atmospheric press.		Additional chlorine under reduced pressure.
	Pressure in mm.	Chlorine (Total=100).		Chlorine (Total=100).		
		Free.	As chloride.	Free.	As chloride.	
Potassium.....	1	0·00	100·00	0·00	100·00	—
Barium .....	1—2	0·066	99·934	0·093	99·907	nil
Calcium .....	4	0·54	99·46	0·58	99·42	nil
Lead .....	20—25	75·3	24·7	48·0	52·0	27·3
Silver .....	3	21·1	78·9	0·2	99·8	20·9
	20	6·75	93·25	0·2	99·8	6·55
Potassium, with 5 per cent. ppd. MnO <sub>2</sub> .....	25—44	0·45	99·55	0·52	99·48	nil
Potassium, with 20 per cent. MnO <sub>2</sub> from nitrate .....	25—45	0·31	99·69	0·31	99·69	nil

Table I gives the averages of the determinations recorded in the present paper together with some of the results previously obtained with pure chlorates (Trans., 1900, 77, 137, 717; 1901, 79, 247). It will be seen that with the chlorates of (potassium) barium and calcium, reduction of pressure causes no increase in the proportion of free chlorine, but in the decomposition of lead chlorate and of silver chlorate, where there is a secondary reaction removing free chlorine from the gaseous products, reduction of pressure results in a large additional quantity of chlorine remaining in the free state, an example of the well-known effect of decrease of the concentration (or pressure) of a gas which is reacting with a solid or liquid. Had the presence of oxides of manganese resulted in the intermediate liberation of the whole of the chlorine in the potassium chlorate (as required by cycles of classes 1 and 2), the behaviour of the mixture should in this respect have been comparable with that of silver chlorate. On the contrary, however, reduction of pressure did not produce the slightest increase in the amount of chlorine remaining free, or, in other words, the production of chloride proceeded to the same extent. There is therefore no secondary reaction removing liberated chlorine, and cycles of classes (1) and (2) are excluded, the changes being limited to oxidation and deoxidation.

*The Origin of the Trace of Chlorine.*—As the free chlorine found in the gas is the actual amount liberated instead of being the vestige of a very large quantity originally evolved, its origin is relatively unimportant. It may, however, be of interest to note that McLeod (1889) found that a mixture of manganese peroxide and sodium chloride evolved chlorine when heated. The oxides  $MnO_2$ ,  $MnO_3$ , and  $Mn_2O_7$  have marked acidic properties towards potash, and must therefore liberate chlorine from potassium chlorate (Baudrimont found that "fused boric acid" expelled a very large proportion with great readiness). These two facts seem to account sufficiently for the production of the trace of chlorine, but there is, in addition, the bare possibility of the formation of traces of chlorate or chloride of manganese from which chlorine would be rapidly expelled.

*Nature of the Substance which actually causes the Facilitation.*—It seems unlikely that the manganese compound, acting as an "oxygen-carrier," should contain chlorine, on account of the smallness of the proportion of free chlorine and the readiness with which chlorine is evolved from chlorate or chloride of manganese. As the amount of liberated chlorine in the gas is so small, only traces of any compound containing potassium and manganese can be present under ordinary conditions, but much more would be formed on adding a little potassium carbonate, which however, greatly retards decomposition (Jungfleisch, McLeod, 1889), or by replacing manganese peroxide by potassium

permanganate but this is actually much less active (Baudrimont ; McLeod, 1889) ; it therefore seems certain that the substance taking part in the cycle is not a potassium compound.

By this process of exclusion, it would appear that the actual oxygen-carriers must be the oxides of manganese. This being so, addition of an alkali would be expected to produce a retardation by converting the most active particles into manganate. The evidence at present available appears to afford only an indication of the probable limits between which oxidation and deoxidation proceed. On heating manganese peroxide with potassium chlorate, the mass becomes purple (as others have observed) provided the amount of the peroxide is not sufficient to obscure such a phenomenon. The author has confirmed this with materials free from iron, and finds that the aqueous extract gives the permanganate absorption spectrum, and that a little sulphurous acid produces a brown precipitate cleared up by excess. Jungfleisch and others regard this production of permanganate as indicating the formation of  $Mn_2O_7$ , but in order to establish such a view it must be shown that the combination with potassium does not precede the oxidation. Manganate predominates when a small proportion of free alkali is added, but the purple colour is momentarily produced each time the mass is reheated after cooling.

*Perchlorate Formation and its Prevention by addition of Oxides of Manganese.*—It appears that no perchlorate is even temporarily formed when potassium chlorate is decomposed in presence of oxides of manganese for, omitting earlier references, Eccles (this Journal, 1876, i, 856) found that none was present in the residue, and McLeod (Trans., 1889, 55, 191) has shown that if once formed it would not be decomposed under the conditions of experiment.

Some have regarded this absence as very remarkable (although hydrochloric acid also brings about the decomposition without forming perchlorate), but the author is not aware of any reason for supposing that the formation of a perchlorate is an *essential* part of the reaction by which oxygen is obtained from chlorates.

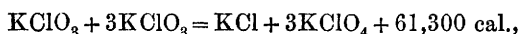
The old equation,  $2KClO_3 = KCl + KClO_4 + O_2$ , which is at last disappearing from text-books, was shown to be incorrect so long ago as 1843 by Marignac (*Berzelius' Jahresber.*, 1845, 24, 192). The more recent work of Frankland and Dingwall (Trans., 1887, 51, 274) and of Teed (Proc., 1885, 1, 105 ; 1886, 2, 141 ; Trans., 1887, 51, 283) shows that for one molecular proportion of perchlorate, from 0.56 to 0.77 molecular proportion of chloride was formed according to the rate and extent of the decomposition. With the chlorates of less basic metals, very much less perchlorate is formed, as may be seen from Potilitzin's work with the chlorates of barium, lithium, strontium, and calcium (Abstr., 1888, 219 ; 1889, 338 ; 1890, 696

1892, 1275). In the case of calcium chlorate, one molecule of perchlorate is formed for about 17 to 20 of chloride, whilst the author has found that lead chlorate yields little or no perchlorate (Trans., 1900, 77, 718). This variation in the proportion of perchlorate renders it difficult to imagine that its formation is due to the breaking down of a large molecule of chlorate containing perchlorate groups (as has been suggested). Further difficulties are the absence of perchlorate when the chlorate is decomposed by treatment with hydrochloric acid, and the fact that potassium perchlorate yields some chlorate when heated, the latter seeming to point to the conclusion (by analogy) that both chlorate and perchlorate have the larger molecule.

The perchlorate is not formed by combination with free oxygen, for reduction of pressure would greatly decrease this reaction and consequently bring about a far more rapid evolution of oxygen, especially in the later stages. No such result is, however, produced (Trans., 1900, 77, 144).

When potassium chlorate is heated with such substances as silver oxide, mercuric oxide, lead peroxide, barium peroxide, &c. (Fowler and Grant, Trans., 1890, 57, 279), it acts as a strong reducing agent, perchlorate being formed by union with the oxygen of these substances. The same authors have also shown that the monoxides of barium, calcium, and lead will act as oxygen-carriers, being first oxidised by the chlorate below its ordinary temperature of decomposition and then reacting with more chlorate, yielding perchlorate without evolution of oxygen.

From this, it will be seen that potassium chlorate can hardly fail to undergo self-oxidation when heated alone, and it seems necessary to conclude that the perchlorate is formed by the reaction



this having no *essential* connection with the decomposition into chloride and oxygen, although it proceeds at a similar temperature.

This theory explains the variation of the proportion of perchlorate, for the rates of the two reactions would not be expected to be equally affected by variation of temperature, and the absence of perchlorate when oxides of manganese are present would be the natural consequence of the addition of a substance which brings about the transformation into chloride and oxygen at a temperature far below that at which the "perchlorate" reaction proceeds with an appreciable velocity.

A short statement of conclusions will be found at the end of the paper.

## EXPERIMENTAL.

A very active specimen of "precipitated manganese peroxide" was prepared by the action of bromine on manganous acetate at about 55°. The precipitate thus obtained is stated to be a hydrate of  $\text{MnO}_2 \cdot 5\text{MnO}_2$ . After prolonged washing, it was dried for 11 hours in an air-oven at 120°, then at 200° for an hour with the pressure reduced to 3 mm., and finally for 1½ hours at 300°, also under 3 mm. pressure. A small trace of water still remained, but the heating was not extended, as it is stated that the precipitated oxides begin to give off traces of oxygen at 210°, although oxygen is often absorbed at lower temperatures.

The substance was in the form of shining, black scales, so bulky that a 1 oz. bottle held only 6 grams. By means of hydrochloric acid and potassium iodide, it was found to contain 31·8 per cent. of "available oxygen," corresponding to 86·6 per cent. of  $\text{MnO}_2$ . The formula  $\text{MnO}_2 \cdot 5\text{MnO}_2$  requires 85·8 per cent. of  $\text{MnO}_2$ .

Another oxide was prepared by a method described by Gorgeu (*Compt. rend.*, 1879, 88, 797). "Pure" manganous carbonate (free from any trace of iron) was added in excess to nitric acid; the fine crystals of manganous nitrate obtained from the solution were drained, carefully rinsed with cold water, heated at 100° for some time, and partially decomposed by heating at 170° for 19 hours. The residue was washed with boiling water, finely ground in an agate mortar, and again thoroughly washed. It was dried at 140° and then heated at 300° for rather more than an hour with the pressure reduced to 3 mm. The product was a dense, glistening black powder, still retaining a trace of water. The available oxygen amounted to 35·8 per cent., corresponding to 97·2 per cent.  $\text{MnO}_2$ .

McLeod (*Trans.*, 1894, 65, 204; 1896, 69, 1017) having published some determinations of the alkalinity of the residues obtained by heating potassium chlorate with manganese peroxide, the author attempted to investigate the evolution of chlorine by titrating the residues, as previously carried out in his study of pure chlorates. Various amounts of the two pure oxides and of two commercial specimens, "ordinary" and "pure artificial" (probably pyrolusite and the residue from heating manganous nitrate respectively), were heated with potassium chlorate. The liberation of chlorine necessitated the formation of quantities of potassium oxide equivalent to 4—24 c.c. of *N*/500 alkali, but on extracting the product with water, taking care to exclude carbon dioxide and decanting the extract in order to avoid absorption of potash by filter paper, no alkalinity could be detected by means of phenolphthalein, although this indicator is sensitive to 1/80 of the least

amount of potash formed. On the contrary, these extracts neutralised from 0.05 to 0.3 c.c. of  $N/500$  potash. If an insoluble residue (0.05 to 0.2 gram of manganese peroxide) was boiled with about 5 c.c. of  $N/500$  potash, the greater part, and in some cases practically the whole, of the potash was absorbed in two minutes. The above procedure was varied by heating the product with water for  $5\frac{1}{2}$  hours and by treating it directly with  $N/500$  potash; in each case, the behaviour was the same. Instead of being alkaline, the extracts are therefore slightly acid.

The above properties of manganese peroxide have been previously observed by Gorgeu (*Ann. Chim. Phys.*, 1862, [iii], 66, 156), and by Wright and Menke (*Trans.*, 1880, 37, 48). In these papers, it is shown, for example, that manganese peroxide carries down potash even when precipitated from a liquid containing 25 per cent. of nitric acid, and that when treated with aqueous potash the amount absorbed is approximately that required for the formation of  $K_2O, 5MnO_2$ .

McLeod employed litmus in his titrations, which were somewhat discordant. It is perhaps only fair to state that in his 1896 paper (p. 1019) will be found the statement that "it is not easy to judge of the identity of the colour of the liquids, and the determinations are not of much value." As pyrolusite was the material employed by him (*ibid.*, p. 1016) it seems possible that the manganese peroxide was saturated with some base, and therefore did not combine with the whole of the potash.

*The Chlorine Evolved at Various Pressures.*—On account of the removal of chlorine by heated glass (*Trans.*, 1900, 77, 139) and the combination of potassium oxide with manganese peroxide (see above), there seems to be no method of ascertaining the exact amount of chlorine evolved unless the decomposition is made sufficiently rapid for the former error to be negligible. In order to study decompositions of the required rapidity, a soda-glass tube containing 1 gram of potassium chlorate and a known weight of manganese peroxide was furnished with an indiarubber stopper, through which passed the stem of a T-piece. One end of the top of the T was connected to a mercurial manometer indicating the pressure under which the decomposition took place, whilst the other was sealed to the tubular stopper of the first of two absorption tubes containing a solution of neutral potassium iodide. The farther limb of the second absorption tube was connected to a Fleuss pump and an exhausted four-gallon stoneware bottle when the decomposition was to take place under reduced pressure, but, for atmospheric pressure, to a tube delivering the gas below a graduated cylinder inverted over water.

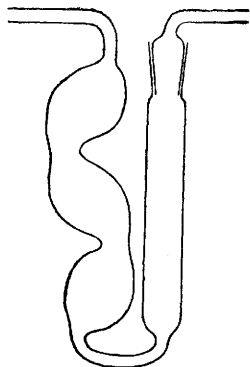
In the first decompositions under reduced pressure, the rapid stream of gas carried much of the potassium iodide solution out of the absorption tubes. This difficulty was overcome by giving the bulbed ascend-



ing limb a marked zig-zag form, as shown in the accompanying figure. A comparatively small tube of this form will pass the full blast of an ordinary foot bellows with the loss of only a few small splashes.

It was not thought necessary to complicate the apparatus by decomposing the mixture in a platinum vessel, as the action of the soda-glass would not appreciably increase the amount of chlorine liberated in presence of manganese peroxide (Trans., 1900, 77, 144).

In conducting an experiment, a bath of melted pewter was raised until the surface was some distance above the level of the mixture in the tube, and the pressure was then noted. After an interval, the temperature was raised until the decomposition became rapid, and the maximum pressure observed, the manometer being tapped meanwhile. In experiments under atmospheric pressure, there was but little increase. After decomposition, the tube was twice exhausted through the potassium iodide solution, which was then titrated with  $N/500$  thio-sulphate. The absorbing arrangements were sufficiently efficient, as comparatively little chlorine reached the second tube.



In the first series (*a*, Table II, p. 1075), 5 per cent. of the precipitated peroxide, approximately  $MnO_2 \cdot 5MnO_3$ , was employed, and the mixture decomposed in a tube of 15 mm. bore and 230 mm. length, simply sealed at one end. The decomposition became rapid and beyond control when the temperature of the bath had risen to *about*  $340^\circ$ . Under reduced pressure, the mass tended to rise in the tube to about the level of the surface of the bath. This would tend to reduce the rise

of temperature, and may explain the slight *decrease* of free chlorine accompanying reduction of pressure.

In series (*b*), more concordant results were obtained, because the rising of the mass was, to a great extent, prevented by decomposing the mixture in a bulb of 28 mm. diameter blown at the end of the tube. Owing to the excessive activity of the precipitated oxide, these decompositions were not so regular as those in the next series.

Ten per cent. of the manganese peroxide, obtained by heating the nitrate, did not readily produce rapid decomposition. In series (*c*), 20 per cent. was employed, and the rush of gas took place when the bath reached a temperature of *about*  $355^\circ$ , and it lasted about half a minute. These decompositions were exceedingly regular, and there is a corresponding agreement among the results. With this oxide, a bulb tube was an absolute necessity.

The duration of the rush of gas is necessarily a somewhat indefinite

quantity on account of the difficulty of deciding the moment at which it begins or ceases to be "rapid." With reduction of pressure, there appeared to be an increase of duration, but this may have been due to an error of judgment in allowing for the visible effect of expansion of the gas. It will be seen from Table II that reduction of pressure did not give the slightest increase in the proportion of free chlorine.

It may be of interest to note that manganese peroxide also facilitates the decomposition of other chlorates. Tubes containing 0.1 gram of the peroxide, prepared by heating manganous nitrate, together with 1 gram of potassium chlorate or the chemically equivalent quantity of the chlorates of barium and calcium, were placed side by side in a fusible metal bath, of which the temperature was raised at a rate averaging about 3° per minute. The decomposition was at first most pronounced in the case of calcium and least in that of potassium chlorate, but the latter was the first to give a rapid stream of gas, and barium the next, whilst the calcium chlorate was completely decomposed without any rush at all. As when heated alone these

TABLE II.—*Potassium Chlorate with Oxides of Manganese.*

Number.	Pressure in mm.	Chlorine (total=100).		Chlorine per 100 parts of		
		As chloride.	Free.	Potassium chlorate.	Manganese peroxide.	
a	52	767	99.46	0.54	0.157	3.13
	54	771	99.53	0.47	0.137	2.74
	57	768	99.51	0.49	0.141	2.82
	51	23—36	99.54	0.36	0.104	2.08
	55	27—39	99.60	0.40	0.117	2.34
	56	27—38	99.63	0.37	0.106	2.11
b	66	763	99.41	0.59	0.170	3.40
	69	764	99.46	0.54	0.156	3.13
	67	24—60	99.41	0.59	0.170	3.40
	68	23—49	99.54	0.46	0.133	2.66
c	63	763	99.689	0.311	0.090	0.45
	64	763	99.684	0.316	0.091	0.46
	62	24—45	99.684	0.316	0.091	0.46
	65	25—46	99.686	0.314	0.091	0.45

Series (a) and (b), 5 per cent. of precipitated manganese peroxide. (a), Tube simply sealed at one end, duration of rush of gas about  $\frac{1}{2}$  minute. (b), Tube with bulb, duration about  $\frac{1}{3}$  minute. (c), 20 per cent. of manganese peroxide from heated nitrate, tube with bulb, duration about  $\frac{1}{2}$  minute.

chlorates differ very greatly in stability, it appears that the properties of manganese peroxide form the dominant factors in conditioning the temperature at which the decomposition takes place, the properties of the chlorate being of less importance.

*Conclusions.*

(1) That the facilitating action of the oxides of manganese is due to the formation of a higher oxide of manganese by the oxidising action of the heated chlorate and the subsequent breaking up of the higher oxide.

(2) That the liberation of chlorine is not an essential part of the cycle of changes bringing about the facilitation.

(3) That when potassium chlorate is heated by itself, perchlorate is formed by self-oxidation, a process not *essentially* connected with the evolution of oxygen.

(4) That addition of manganese peroxide prevents the production of perchlorate by bringing about the decomposition into chloride and oxygen at a temperature much below that at which self-oxidation of the chlorate proceeds at an appreciable rate.

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