XXXI.—*Potassium Chlorate and Perchlorate.*

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THE results published in the preceding paper by Dr. Percy Frankland and Mr. Dingwall in the main corroborate those obtained by me. Short abstracts of my two papers on this subject appear in the "Proceedings" Nos. 12 and 16 of 1885–86.

Frankland and Dingwall give the equation $8KClO_3 = 5KClO_4 + 3KCl + 2O_2$ as representing the course of the reaction when potassium chlorate is heated over a naked flame, and point out that their results tally better with this equation than with the equation $10KClO_3 = 6KClO_4 + 4KCl + 3O_2$, which I originally suggested. They omit, however, all reference to the equation proposed in my second paper ("Proceedings" No. 16), $22KClO_3 = 14KClO_4 + 8KCl + 5O_2$, whereas if my two equations are added together, and the resulting equation reduced to its lowest terms (dividing by four), it gives the equation $8KClO_3 + 5KClO_4 + 3KCl + 2O_2$, proposed by Frankland and Dingwall, which is merely one of an indefinite number of equations within the limits of my two.

I may point out that when the decomposition is fairly brisk, the results agree more nearly with the equation $10KClO_3 = 6KClO_4 + 4KCl + 3O_2$, and it is noteworthy that in this equation the amount of oxygen that is evolved in the free state is equal to the amount that goes to form perchlorate.

There seems to be an idea that in order to construct an equation representing the decomposition, data are required other than the determination of the evolved oxygen and of the potassium chloride produced, and that it is necessary to determine directly the perchlorate formed, or at all events the undecomposed chlorate. This is erroneous, for it is obvious that for every 74·5 parts of potassium chloride formed, there must have been 122·5 parts of potassium chlorate decomposed, and of the 48 parts of oxygen thereby eliminated, what is not evolved in the free state *must* have gone to form perchlorate. Any direct determinations of the potassium chlorate and perchlorate are therefore unnecessary, but would form a most rigorous test of the accuracy of any process for determining chlorates in presence of perchlorates. From this it will be seen that the data I employed are as sufficient for the determination of the perchlorate formed and of the remaining undecomposed chlorate as the determination of the oxygen lost when copper oxide is heated in hydrogen, and of the water formed, are for ascertaining the composition of water. To give the results in my second paper,* I found that when the chlorate was very gently heated, the products obtained agreed more nearly with the $22KClO_3$ equation, which demands 20 of oxygen to 74·5 of potassium chloride. In order to give some idea of what I mean by gentle heating, I may state that it took an hour and a quarter to evolve the 1·27 per cent. of oxygen in Experiment No. 2.

No.	$KClO_3$ taken, in grams.	Oxygen evolved, per cent.	KCl formed, per cent.	Amount of oxygen to 74·5 of KCl.
1......	4·3782	3·60	11·58	23·16
2......	6·865	1·27	4·73	20·00
3......	9·291	1·61	6·00	19·99
4......	4·759	1·60	6·14	19·41
5......	4·4905	1·47	4·84	22·63
6......	6·050	0·80	2·18	27·34

In Experiment No. 6 the chlorate was heated strongly for a very short time, so as to demonstrate that the results varied according to the treatment rather than according to the amount of oxygen evolved.

As Frankland and Dingwall thought that when the chlorate was heated over the naked flame, there was a considerable risk of decomposing the perchlorate formed, they made experiments where the chlorate was heated in sulphur vapour; but under these circumstances they obtained less perchlorate than when the naked

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* The paper was not published in full, and the data do not appear in the Proceedings.

flame was employed. They also give the result of an experiment in which a mixture of the chlorate with powdered glass was heated in sulphur vapour; this yielded much less perchlorate than in any other of their experiments. It is difficult to reconcile this with the stability of perchlorate under these particular conditions. I have shown that powdered glass does not affect the decomposition of the chlorate. In one experiment, I took 3·660 grams of potassium chlorate, mixed with 1·697 grams of powdered glass, and heated the mixture until 4·29 per cent. oxygen was lost, and 12·49 per cent. of potassium chloride formed. By calculation, the resulting products were—

$KClO_3$.	$KClO_4$.	KCl.	O.
50·67	32·55	12·49	4·29 = 100

with a ratio of KCl : O = 74·5 : 25·59.

I do not in the least dispute Frankland and Dingwall's results as to the stability of the perchlorate heated *per se* in sulphur vapour, but in the light of my experiment with powdered glass I think their result tends to show that a solution of perchlorate in chlorate and chloride is decomposed at that temperature.

In leaving the subject of the chlorate, I may repeat what I said in my former paper, that no equation can be given which represents the decomposition of potassium chlorate when heated, and only proposed the two I have submitted as marking the usual limits of the reaction.

The results of the decomposition of the perchlorate by heat given in my second paper were—

No.	Amount of $KClO_4$ taken, in grams.	Oxygen evolved, per cent.	KCl formed, per cent.	Amount of oxygen to 74·5 of KCl.
1......	2·4355	3·10	2·97	77·76
2......	3·8825	4·47	4·41	75·59
3......	1·850	7·30	7·82	69·55
4......	1·217	35·21	40·33	65 04

Frankland and Dingwall have lost the first high ratios of oxygen to potassium chloride by driving off too much oxygen, so that their results are incomplete. It is obvious that potassium perchlorate, if it loses more oxygen than is expressed by the equation $KClO_4 = KCl + 2O_2$, must be forming a lower oxide of potassium chloride (if I may be allowed to use such an expression), and the only oxide possible under the circumstances is the chlorate. This, as I stated in the discussion on the reading of my second paper (January 21st, 1886), was further corroborated by adding a drop of sulphuric acid to the product, neither perchlorate nor a mixture of perchlorate with chloride giving the peculiar yellow produced by the chlorate. No other explanation than the formation of chlorate being possible, and its presence being further demonstrated by this direct test, I consider that I fully proved its formation, Messrs. Frankland and Dingwall's experiments merely confirming the results I had already obtained.

In my second paper I also showed that no chlorate was formed on heating perchlorate with manganese binoxide. The following are the results:—

$KClO_4$ taken, grams.	MnO_2 taken, grams.	Oxygen evolved, per cent.	KCl formed, per cent.	Amount of oxygen to 74·5 of KCl.
1·2305	1·409	14·87	17·22	64·33
1·841	2·5985	5·35	6·24	63·87

In carrying out these experiments, I estimated the oxygen by loss of weight and the potassium chloride by standard silver nitrate solution with potassium chromate as indicator, and used a small stoppered retort as the decomposing vessel, keeping back all fumes by a cotton-wool plug. I consider that it is far better to employ a retort than a tube, because with the former in experiments of this character, it is very easy to displace rapidly all the oxygen by air before weighing, whereas in a plugged tube a very appreciable time must be allowed to elapse before the oxygen can diffuse out.*

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* As the capacity of the tubes employed by Messrs. Frankland and Dingwall in their experiments was only about 10 c.c., the error introduced from imperfect removal of the oxygen by diffusion would be inappreciable; even supposing there were no diffusion whatever, the increase in weight would not amount to more than 0·0006 gram, when it is remembered that air must enter through the plug as the tube cools.—[EDITOR.]