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XXX.—*The Decomposition of Potassium Chlorate and Perchlorate by Heat.*

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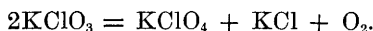
SOME interesting points in connection with the decomposition of potassium chlorate by heat were raised by Teed in a paper, the abstract of which was published in the Proceedings of the Society (No. 12, 1885-86). At the suggestion of Professor Thorpe, we

have submitted these points to further examination, and have also investigated the behaviour of the perchlorate under the action of heat.

In the first series of experiments brought before the Society by Dr. Teed, he pointed out that when potassium chlorate is heated it first undergoes decomposition according to the equation—



and not according to the commonly accepted one—



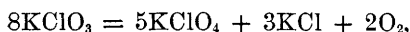
In these experiments no special method of heating the chlorate was adopted with a view to maintain a constant temperature, and only the loss (calculated as oxygen evolved) and the chloride formed were determined.

In repeating these experiments, we have not only determined the loss and the chloride formed, but also the chlorate remaining unchanged, and we have adopted special precautions to prevent any loss through spurting by plugging the tube in which the decomposition was effected with glass-wool. In some experiments, we have also preserved a constant temperature during the decomposition by placing the tube in the vapour of boiling sulphur instead of heating it with a naked flame.

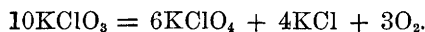
The potassium chlorate remaining undecomposed after the operation was determined by reducing it with the zinc-copper couple in the manner described by Thorpe (*Chem. Soc. Journ.*, 1882, 547), and then determining the increase in chloride by titration with decinormal silver nitrate, using potassium chromate as indicator.

In these experiments, the following results were obtained (see Table I, p. 276).

In the case of the first two of the experiments recorded above, it will be seen that although very different quantities of oxygen were driven off in the two cases, yet the proportion on the potassium chlorate actually decomposed is almost exactly the same. Moreover, in the quantity of oxygen liberated, and in the chloride and perchlorate formed, the decomposition in each case coincides very closely with the requirements of the equation—



the coincidence with this equation is far greater than with the more complex equation suggested by Teed—



In the third experiment, however, in which a larger quantity

I. *Potassium Chlorate heated over Naked Flame.*

Percentage of oxygen evolved on weight of KClO_3 taken.	On KClO_3 actually decomposed.			
	Percentage of oxygen evolved.	KCl formed (per cent.).	KClO_4 formed (per cent.).	Proportion of oxygen evolved to 74.57 parts of KCl formed.
No. 1. 2.66	6.30	22.48	71.22	20.87
No. 2. 5.19	6.27	22.43	71.30	20.84
No. 3. 6.47	7.09	23.68	69.23	22.32
Equation—				
$10\text{KClO}_3 = 6\text{KClO}_4 + 4\text{KCl} + 3\text{O}_2$ requires	7.83	24.34	67.83	24.00
$8\text{KClO}_3 = 5\text{KClO}_4 + 3\text{KCl} + 2\text{O}_2$ requires	6.53	22.81	70.66	21.33
$2\text{KClO}_3 = \text{KClO}_4 + \text{KCl} + \text{O}_2$ requires	13.05	30.42	56.53	32.00

of oxygen was driven off, the results fall intermediate between the 8KClO_3 and the 10KClO_3 equations.

It thus appears that the equation representing the decomposition varies as the latter is more or less complete.

As in the above experiments, as well as in those of Teed's, there is no guarantee that the reaction is not complicated through the further decomposition by the naked flame of perchlorate at first formed, it appeared to us desirable to ascertain the nature of the decomposition taking place at a temperature below that at which potassium perchlorate is decomposed.* For this purpose we selected the temperature of boiling sulphur.

The piece of combustion-tubing containing the potassium chlorate was fitted by means of a cork into the tubulure of a retort in which a quantity of sulphur was kept in ebullition, so that the portion of the tube containing the chlorate was completely surrounded by the sulphur-vapour.

In other cases we simply fitted, by means of glass-wool, the tube with chlorate into a boiling tube containing sulphur.

* 4.8208 grams of potassium perchlorate, containing 1.35 per cent. of potassium chlorate (as indicated by the zinc-copper couple reaction), were heated for 56 hours in sulphur vapour, and found to lose only 0.0149 gram or 0.3 per cent.

Two of these experiments were carried on simultaneously, the tubes being weighed daily in order to ascertain whether decomposition was still proceeding. The decomposition, which at first was comparatively active, gradually became very sluggish indeed. Thus in the two parallel experiments, in one case 5·3345 grams of chlorate were exposed to the heat of the sulphur-bath for 98 hours, and during the first five hours the loss amounted to 0·1166 gram (2·18 per cent.), whilst in the last five hours the loss amounted to only 8 mgrms., and in the other case 2·5149 grams of chlorate were heated for 79 hours, and lost during the first seven hours 0·0686 gram (2·72 per cent.), and during the last five hours only 0·2 mgrm.

The residues were treated as before described in the case of the naked flame experiments, and the following results were obtained :—

II. *Potassium Chlorate heated in Sulphur-vapour.*

Percentage of oxygen evolved on weight of KClO_3 taken.	On KClO_3 actually decomposed.			
	Percentage of oxygen evolved.	KCl formed (per cent.).	KClO_4 formed (per cent.).	Proportion of oxygen evolved to 74·57 parts of KCl formed.
No. 1. 6·89	8·14	25·44	66·42	23·88
No. 2. 6·78	8·76	26·03	65·21	25·10
No. 3. (KClO_3 mixed with powdered glass) 14·30	15·34	33·55	51·11	34·10

In all three cases, the decomposition of the chlorate was incomplete, for in each case the residue contained unchanged chlorate as well as the chloride and perchlorate formed by the decomposition of the original salt.

It will be seen that in experiments Nos. 1 and 2 the decomposition had gone further than is indicated by the 8KClO_3 equation, No. 1 agreeing fairly well with the 10KClO_3 equation, whilst in No. 2 the decomposition had gone even beyond that.

It is especially noteworthy that when the chlorate was mixed with half its weight of powdered glass the decomposition of the chlorate was almost complete, and that it took place more nearly according to the old equation, $2\text{KClO}_3 = \text{KClO}_4 + \text{KCl} + \text{O}_2$.

It would appear, therefore, that when potassium chlorate is partially decomposed by heat, the decomposition takes place according to equations of the type $8\text{KClO}_3 = 2\text{O}_2 + 5\text{KClO}_4 + 3\text{KCl}$, and

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that the more complete the decomposition is the more does it approximate to that indicated by the equation



Decomposition of Potassium Perchlorate.

In Dr. Teed's second communication on potassium chlorate (Proc., 1885-86, p. 141), he incidentally mentions that, in the decomposition of potassium perchlorate by heat, potassium chlorate is at first formed. This point appeared to us of particular interest as being opposed to Berthelot's "principe du travail maximum" (*Essai de Mécanique Chimique, fondé sur la thermochimie*, 2, 421, 1879), which asserts that every chemical change taking place without the intervention of any foreign energy tends to the production of that body or system of bodies which generates the greatest amount of heat. Now, as is well known, in the production of potassium chlorate a large amount of heat is absorbed which is subsequently liberated in its decomposition.

As the only evidence adduced by Teed in support of this production of potassium chlorate, was the liberation of a larger quantity of oxygen, in proportion to the potassium chloride formed, than is required by the equation



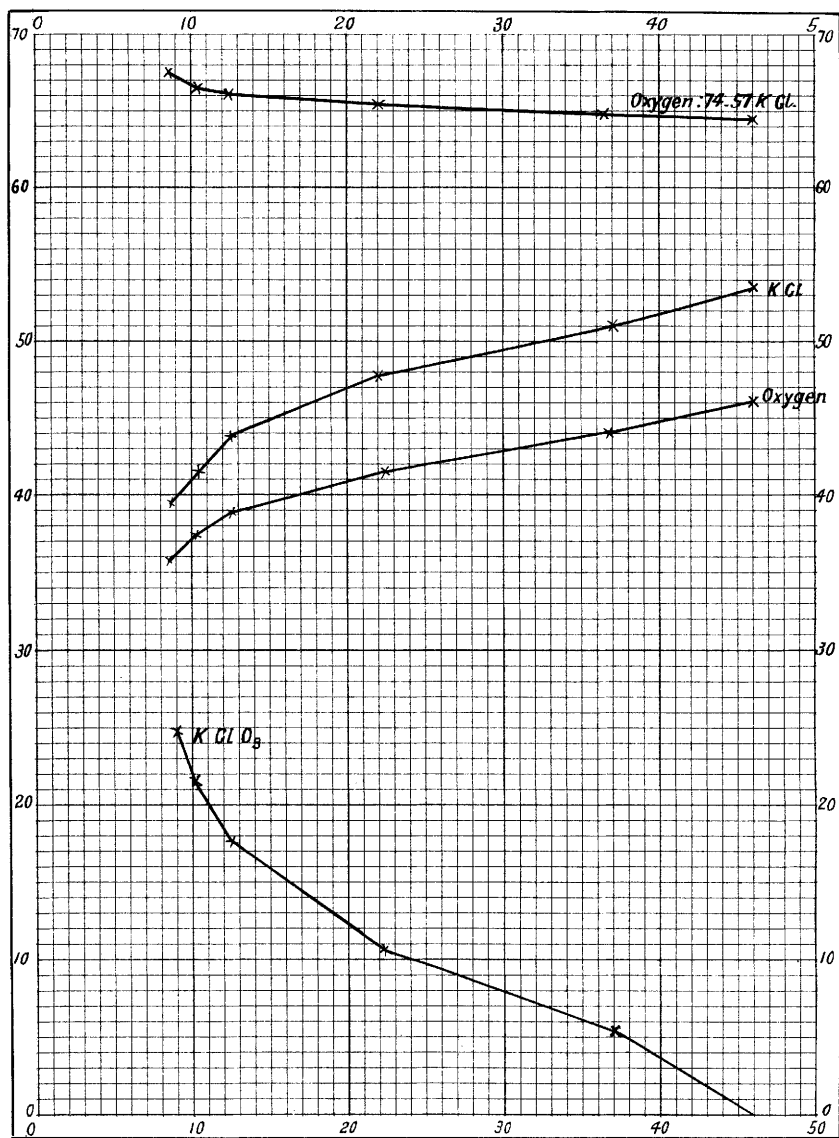
it appeared to us desirable to place this interesting formation of potassium chlorate on a surer foundation.

For this purpose the following experiments were undertaken:—

The potassium perchlorate which we first employed, although the purest commercially procurable, was found by means of the zinc-copper couple reaction to contain 1.35 per cent. of potassium chlorate.

Portions of this potassium perchlorate were heated over a naked flame in a piece of combustion-tube sealed at one end and loosely plugged with glass-wool at the other. The heating was continued so as to liberate a different proportion of oxygen in each experiment. In each case, the residue was dissolved in water, the chloride determined by means of decinormal silver nitrate in one portion, and in another the increase in chloride obtained by reduction with zinc-copper couple was ascertained and calculated as chlorate. In this manner, the following results were obtained (see table, p. 279).

Excluding experiment No. 2, it will be seen that the results form a continuous series, the proportion of chlorate formed diminishing as the oxygen liberated increases, whilst the chloride formed increases with the proportion of oxygen evolved. The relationship between

*Journ. Chem. Soc. March 1887.***DECOMPOSITION OF POTASSIUM PERCHLORATE BY HEAT.**

Harrison & Sons, Ltd., 5, Mark Lane W.C.

Decomposition of Potassium Perchlorate.

Percentage of oxygen evolved on weight of KClO_4 taken.	Results on potassium perchlorate decomposed.			
	Oxygen evolved (per cent.).	KCl formed (per cent.).	KClO_3 formed (per cent.).	Oxygen to 74·57 parts of KCl formed.
No. 1. 8·77	35·69	39·46	24·85	67·44
No. 2. 9·76	37·37	40·96	21·67	68·04
No. 3. 10·17	37·06	41·48	21·46	66·61
No. 4. 12·53	38·84	43·67	17·49	66·32
No. 5. 22·12	41·76	47·61	10·63	65·41
No. 6. 36·81	44·01	50·72	5·27	64·71
The equation—				
$\text{KClO}_4 = \text{KCl} + 2\text{O}_2$ requires	46·19	53·81	—	64·00
No. 7. Potassium perchlorate and MnO_2 heated in sulphur vapour until of constant weight 46·98	46·98	52·65	—	66·54

the three products of decomposition is rendered most apparent by means of the accompanying diagram, in which the abscissæ represent the percentages of oxygen evolved on the weight of perchlorate taken, whilst the ordinates serve to indicate respectively the proportions of potassium chlorate, chloride, and oxygen formed on the weight of perchlorate actually decomposed, as well as the proportion of oxygen liberated to 74·57 parts of potassium chloride formed. In experiment No. 7, a mixture of potassium perchlorate and peroxide of manganese was heated in sulphur vapour until no further loss in weight took place. In this case, the decomposition of the perchlorate to chloride and oxygen was complete, the slight divergence from the requirements of the equation being due to the evolution of a little chlorine, the odour of which was distinctly perceptible at the commencement of the decomposition. On this account, the oxygen evolved (calculated directly from the loss in weight) is above the theoretical, the chloride below, and consequently the proportion of oxygen to chloride markedly above that indicated by the equation.

As in the above experiments the evidence that potassium chlorate is formed was still somewhat indirect, being dependent on the differential result obtained by the action of the zinc-copper couple, we proceeded to prove its formation more directly by partially decom-

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posing a considerable quantity of the same perchlorate and then obtaining the chlorate from the residue by fractional crystallisation.

For this purpose about 47 grams of potassium perchlorate (containing 1·35 per cent. of potassium chlorate) were heated in four separate portions so that each suffered a loss of about 10 per cent. The residues were then united, dissolved in water, and submitted to fractional crystallisation; eventually the following eight fractions were obtained, each of which was qualitatively tested for chloride with silver nitrate, and for chlorate with hydrochloric acid:—

Fraction No. 1.—No perceptible chlorate reaction, but very slight opalescence with silver nitrate.

Fraction No. 2.—No perceptible chlorate reaction, but distinct reaction with silver nitrate.

Fraction No. 3.—Very decided chlorate reaction.

Fraction No. 4.—Ditto.

Fraction No. 5.—Ditto, but not quite so strong.

Fraction No. 6.—No chlorate reaction, but copious precipitate with silver nitrate.

Fraction No. 7.—Ditto.

Fraction No. 8.—Ditto.

Fractions Nos. 3, 4, and 5 were then submitted to analysis, with the following result:—

	No. 3.	No. 4.	No. 5.
KCl	2·60	48·29	82·62
KClO ₃	41·68	42·91	14·58
KClO ₄	55·72	8·80	2·80
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

These results leave absolutely no doubt as to the presence of potassium chlorate in the residue from the partial decomposition of the perchlorate, and, moreover, assuming that the whole of the chlorate originally present in the perchlorate as an impurity had remained undecomposed during the heating, this would account for only 0·6416 gram KClO₃ in the residue, whilst the total quantity of KClO₃ found in the above three fractions submitted to analysis amounted to 1·4771 gram, or to 3·1 per cent. of the potassium perchlorate operated on.

In order, however, to render the proof still more complete, we endeavoured to obtain some perchlorate practically free from chlorate altogether, and for this purpose we twice recrystallised the sample of perchlorate used in the former experiments. In order to test the freedom of this perchlorate, thus obtained, from chlorate, we evapo-

rated weighed quantities of it with dilute hydrochloric acid on the water-bath to dryness, then dissolved in water, and again took to dryness, and repeated this operation once more in order to ensure the expulsion of all the excess of hydrochloric acid. Since the perchlorate was proved to be absolutely free from chloride in the first instance, any chloride now present must have been derived from the decomposition of chlorate by the hydrochloric acid added. Two gravimetric determinations of the chloride thus formed by evaporation with hydrochloric acid, showed the presence of potassium chlorate in the purified perchlorate to the extent of—

	I.	II.
KClO ₃ per cent.	0·29	0·21

This perchlorate was thus practically free from chlorate.

N.B.—The zinc-copper couple method was not employed for determining this trace of chlorate for reasons which are apparent from the note appended to this paper.

With this purified perchlorate, a series of decomposition experiments was made similar to that above described, with the exception that the chlorate was determined by evaporation with hydrochloric acid, instead of by means of the zinc-copper couple reaction.

The following results were obtained :—

Decomposition of Potassium Perchlorate (2nd Series).

Percentage of oxygen evolved on weight of KClO ₄ taken.	On KClO ₄ decomposed.			
	Oxygen evolved (per cent.).	KCl formed (per cent.).	KClO ₃ formed (per cent.).	Oxygen evolved to 74·57 parts of KCl formed.
No. 1. 6·34	36·54	38·70	24·76	70·41
No. 2. 7·80	36·63	38·79	24·58	70·42
No. 3. 24·05	43·60	49·21	7·19	66·06
The equation— 7KClO ₄ = 2KClO ₃ + 5KCl + 11O ₂ requires	36·29	38·44	25·27	70·40

The results of experiments I and II agree very closely with the requirements of the equation $7\text{KClO}_4 = 2\text{KClO}_3 + 5\text{KCl} + 11\text{O}_2$, whilst in No. III the decomposition had been carried very much

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further. These results substantiate those previously made with the less pure samples of perchlorate, and thus the formation of potassium chlorate is demonstrated beyond doubt.

Note on the Action of the Zinc-copper Couple on Potassium Perchlorate.

In attempting to estimate the small proportion of chlorate in the purified potassium perchlorate, the results of duplicate determinations were found to vary considerably. This could only be accounted for on the supposition that by the prolonged action of the zinc-copper couple on the perchlorate a small quantity of the latter had become decomposed. That this actually takes place was clearly proved by the following experiments:—

I. A solution of 5.8057 grams of the purified perchlorate was boiled for one hour with the couple, then allowed to stand over night, the liquid being again heated up on the following morning, and the couple then filtered off. By gravimetric determination, a quantity of chloride was found corresponding to 0.77 per cent. of KClO_3 .

II. A solution of 3.2251 grams of the same perchlorate was boiled for two hours with the couple and then immediately filtered. Gravimetric analysis showed the presence of chloride corresponding to 0.65 per cent. of KClO_3 .

III. A solution of 1.0422 grams of the same perchlorate was boiled with the couple for two hours, then allowed to stand over night, then heated up again on the following morning and filtered. The chloride found corresponded to 1.48 per cent. of KClO_3 .

IV. A solution of 5.0447 grams of the same perchlorate was treated side by side with No. III in precisely the same way. The chloride found corresponded to 1.28 per cent. KClO_3 .

V. A solution of 5 grams of the same perchlorate was boiled with the couple for about three hours on December 11th, 1886. The liquid was allowed to stand over till December 13th, when it was boiled for five hours with the same couple, the latter was then filtered off and a new couple added, with which the solution was again boiled. On December 14th it was again boiled all day with the same couple. On December 15th it was boiled with a new couple. On December 16th the boiling with the same couple was continued. On December 17th the solution was boiled with a new couple. On December 18th the boiling was continued with the same couple (the fourth), the liquid was then filtered and the chloride gravimetrically determined, the latter corresponded to 2.49 per cent. of KClO_3 .

It thus appears that by the continued action of the couple, especially

when the latter is renewed, the perchlorate undergoes partial and very slow reduction to chloride.

That this action has not materially affected the results recorded in this paper is clear from the fact that the second series of experiments made with the perchlorate substantiate the first, although in the second series the zinc-copper couple method was not resorted to for the determination of the chlorate, the proportion of the latter being ascertained by decomposition with hydrochloric acid, which has no action on potassium perchlorate.
