142. *The Thermal Decomposition of Potassium Perchlorate.*

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The thermal decomposition of potassium perchlorate *in vacuo* and under small pressures of nitrogen has been investigated between 530° and 550°. Three methods were used, all of which gave results of poor reproducibility. *In vacuo*, chlorine as well as oxygen is produced by the decomposition, but it is absent when an inert gas is present. Potassium chlorate is produced during the decomposition and melting takes place. The results are not in complete agreement with recently published observations by Glasner and Simchen and it is suggested that this may be due to their use of impure crystals.

THE decomposition of potassium perchlorate has been the subject of many researches. Teed (*J.*, 1887, **51**, 283) found that chlorate as well as chloride was formed, and stated that a solution of potassium perchlorate in potassium chlorate and chloride is decomposed at the boiling point of sulphur. Otto and Fry (*J. Amer. Chem. Soc.*, 1923, **45**, 1134) found neither chlorate nor chlorine in their reaction products. Crespi and Caamano (*Anal. Soc. Fís. Quím.*, 1936, **34**, 320, 901) found the addition of chloride to accelerate the reaction, which they suggested was autocatalytic. Hoffmann and Marin (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1932, **27**, 3) carried out an extensive study of both the formation (from chlorate) and the decomposition of potassium perchlorate and studied the effect of additions of other substances. Most of the early work was done at atmospheric pressure in air. Sodeau (*J.*, 1900, **77**, 937) appears to have been the first to notice that small amounts of chlorine are produced in the decomposition of the chlorate. Since the commencement of the present work, Glasner and Simchen (*Bull. Soc. chim.*, 1950, **18**, 233) have reported data for a study of the decomposition of potassium perchlorate, *in vacuo*, at 480—540°. In all cases the rate-time curves showed two maxima, and by making interrupted runs, it was found that the maximum amount of chlorate corresponded to the minima in the rate curves.

EXPERIMENTAL

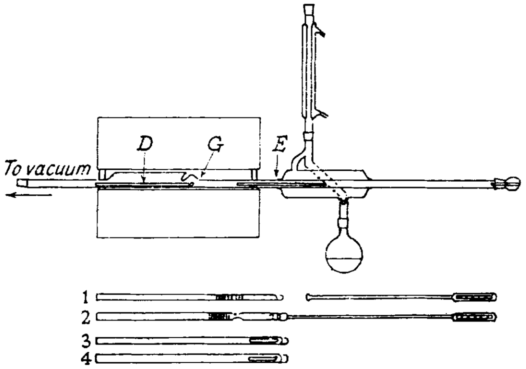
Materials.—From Hopkin and Williams's pure potassium perchlorate, three samples were prepared: "A" was recrystallised four times from water, "B" and "C" five times. A sample "An" was prepared from "AnalaR" potassium carbonate and "AnalaR" 72·7% perchloric acid. The solution of potassium carbonate was made just acid, boiled, and filtered hot, and the crystals obtained on evaporation and cooling were recrystallised four times. The samples all gave negative tests for chloride and chlorate ion. They also appeared to be free (spectroscopically) from traces of sodium.

Experiments were made with: (i) Sample A, ordinary crystals, sieved and graded crystals, and crushed crystals; (ii) sample B, crushed crystals; samples C and An, crushed, graded crystals. Crystals were graded with B.S.S. sieves and were all stored in a vacuum-desiccator over P_2O_5. Crushing can best be described as squeezing the crystals in a mortar with a pestle, circular motion being avoided.

Apparatus.—The apparatus was almost identical with that used by Bircumshaw and Edwards (*J.*, 1950, 1800) with the following addition. To ensure that the material was perfectly dry, a drying unit was incorporated in the vacuum line (Fig. 1). It was arranged that the reaction tube *E* lay in the line surrounded by the outer jacket before being pushed into the reaction vessel at position *D*. It was heated in position *E* for 1 hour and then pushed into the furnace. Water was the usual heating liquid. The reaction tube was approx. 7″ long and was introduced into the furnace by a magnetic "pusher" (Fig. 1, No. 1). If it were required to remove the tube from the furnace during the reaction, type 2 was used. Other types of reaction tube are shown in 3 and 4. A long tube was necessary, for otherwise, traces of potassium chloride would sublime out of it. In types 1 and 2 a glass-wool plug was used to "contain" the perchlorate in the tube. After a run it was usually found to contain some embedded potassium chloride. In some experiments the reaction tube and vapour jacket were tilted at 15° to the horizontal in the hope that the melted decomposition products would remain at one end of the tilted tube. A chromel–alumel thermocouple was introduced into the socket *G*. The method of measuring rates can best be illustrated by recording a sequence of measurements, time (t) being in seconds : $t = 0$, pressure (I) in line measured with pumps in operation; $t = 30$, pumps shut off from line; $t = 60$, pressure (II) in line measured and pump switched on; $t = 120$, pressure (III) in line recorded. The rate pressure was taken as (II) $- \frac{1}{2}[(\text{I}) + (\text{III})]$. For " accumulatory " runs, the line was first evacuated, the pumps were shut off, and the increase in pressure on heating the salt was measured at regular intervals. The total volume of the apparatus was about 2850 c.c.

Results.—0·035 g. was found to be a suitable quantity of the perchlorate. Runs on the uncrushed and ungraded crystals showed considerable divergences. The crystals were then graded into two groups : A_1, bigger than 100 mesh; A_2, 100—150 mesh. Differences were still apparent. Decomposition took approx. 100 min. at 553° (Fig. 2). The appearance of the residue indicated that melting had taken place. The presence of chlorate (m. p. 370°) was confirmed in an interrupted run. The melting may therefore be connected with the formation to some extent of a ternary eutectic of these three salts.

FIG. 1.



It was thought that the differences observed might have been caused by the presence of small amounts of occluded solvent. A new sample of salt was therefore crushed as previously described, and dried in a desiccator; runs were carried out at 541° but showed no greater agreement (Fig. 2). The effect of drying the crystals in an evacuated vessel at 65° (P_2O_5) was investigated and also drying by prolonged pumping in the line, but little improvement was observed.

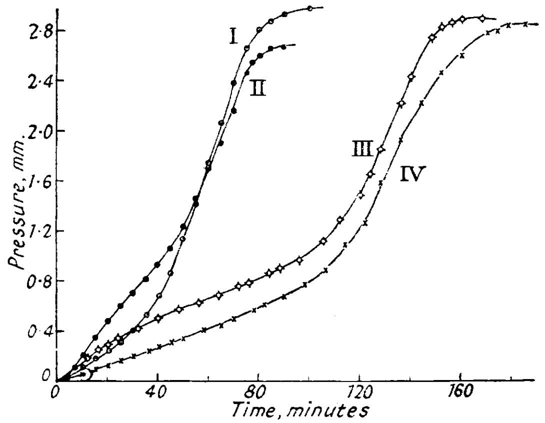


FIG. 2.

I, II, *Sample A, crystals of mesh* 100—150. *Temp.*, 553°.

III, IV, *Sample B, crushed, ungraded. Temp.*, 541°.

Sample C was prepared and sieved into five portions of mesh sizes : $C_a \pm 100$, C_b 100—150, C_c 150—200, C_d 200—300, $C_e < 300$. The preliminary drier was incorporated into the line and by means of the hook attachment (Fig. 1, No. 2) the contents of the tube were examined at various stages of the decomposition. It was found that during the first part of the reaction the solid gradually melted, the crystals first becoming " sticky " in appearance and finally coalescing. When this occurred gas evolution became much more rapid. The tube then contained a bubbling liquid which still had some lumps until the time when the maximum rate was reached whereupon the liquid became homogeneous. The liquid was splashed a considerable way along the tube by the bubbles of gas. Trials of several types of tube to prevent this occurring were unsuccessful. The sublimate was separated from the main bulk of the residue by a clear zone, on which there was no deposit.

Finally, the sample An (from perchloric acid) was sieved to 30—32 mesh and those crystals used at 536° but with no better agreement. The reaction vessel was then tilted at 15° to the horizontal to avoid the spreading of the molten liquid but without effect.

Some " rate " runs were made on 0·080 g. of salt at 540°. The maximum rate occurred at a different time for every sample. The total time for reaction was of the same order as that for an accumulatory run (Fig. 3).

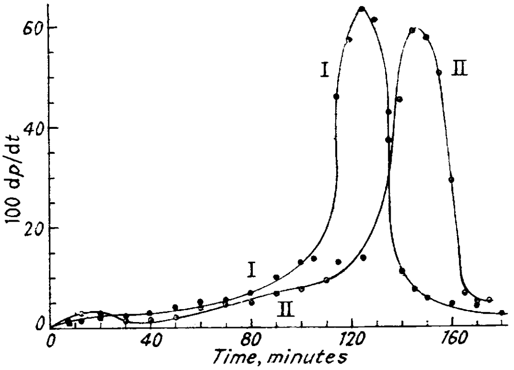


FIG. 3.
Sample An, mesh 30—52. Temp., 541°.
I, II, *Pure material.*

Two runs were made on crystals which had been obtained from a solution containing a considerable amount of potassium chloride. In curves for these two maxima were observed, the second being 2—3 times the height of the first (Fig. 4). Analysis of the salt showed that it contained 1·6% of chloride. Addition of solid chloride to perchlorate (0·005 g. to 0·075 g.) resulted in a much more rapid reaction, again with two maxima (Fig. 4).

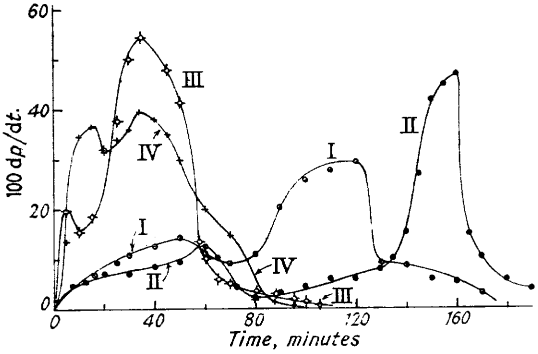


FIG. 4.
I *and* II, *Sample recrystallized from potassium chloride solution. Temp.,* 541°.
II *and* IV, *Sample mixed with solid potassium chloride. Temp.,* 541°.

The amount of chlorine given off was estimated by addition of potassium iodide solution and titration with standard N/100-arsenite from a micro-burette :

Wt. of $KClO_4$, g.	Loss, g.	Decompn., %	Cl, g.	Cl, %	pH of water	pH of solution
0·2000	0·0828	89·7	0·00045	0·87	5·98	6·83
0·1993	0·0854	92·7	0·00049	0·96	5·02	6·06

Chlorine is expressed as a percentage of the total weight of chlorine in the original sample. The residue was dissolved in distilled water and the solution made up to 50 c.c. in the first case and 25 c.c. in the second. The solution was then tested for alkalinity, and the pH values are as given above.

An attempt was made to estimate the chloride : chlorate ratio at the maximum decomposition rate. This could not be done very accurately as it was impossible to predict exactly when the maximum rate would occur. The experiments were made by taking rate measurements of the

Orig. $KClO_4$, g.	Time and temp. of decompn.	KCl, g.	$KClO_3$, g.	Loss in wt., g.	$KCl/KClO_3$ (w/w)
(1) 0·0814	134 min. at 540°	0·031	0·013	0·028	2·37
(2) 0·0800	146 „ 540	0·022	0·014	0·022	1·59

decomposing material, and when the rate was approximately that of the maximum of previous runs the tube was removed and the contents analysed. The chloride ion was determined gravimetrically, and chlorate ion reduced with sulphur dioxide. The perchlorate ion is, of course, not reduced by sulphur dioxide.

Investigation of the Thermal Decomposition of $KClO_4$ *by Use of a Quartz Spiral Spring Balance.*—The construction of the balance will be described in another paper. The initial experiments were carried out on 50-mg. portions of the salt. The first experiment showed that when the evolved gases were continuously removed by pumping, and the pressure in the apparatus thus kept very low, the amount of residue lost on to the sides of the reaction vessel and on to the suspension fibre was considerable. The readings taken of the extension of the spring were thus meaningless. Further experiments were performed on 100-mg. portions, an initial small pressure of nitrogen being introduced into the apparatus and the evolved gases being allowed to accumulate therein. In this way sublimation was considerably reduced but not completely eliminated. The curves of weight loss–time were of a similar type at 530°, but, as with the experiments using pressure measurements, the variation from one sample to the next was considerable. There was, however, a fair agreement during the first part of every run, before the rapid acceleration of the rate took place.

The effect of varying the initial pressure of nitrogen was investigated. The variations between the runs were no greater than those observed with a constant nitrogen pressure. The pressures used were 1·4, 2·7, 10·8, and 10 cm. The most striking difference between these experiments and the previous pressure-measuring ones was that, with the exception of the first experiment, no chlorine was given off during the decomposition. This would explain why Otto and Fry (who worked at atmospheric pressure) did not observe the gas in their work on the perchlorate decomposition; its non-observance by Glasner and Simchen is not understood. The appearance of chlorine is prevented by an inert gas, which would suggest that the sublimation process and the production of chlorine are somehow related. Alternatively, they may be separate processes on which the nitrogen has the same effect, *viz.*, the prevention of the diffusion of the chlorine or potassium chloride vapour from the reaction mixture.

The composition of the contents of the bucket when melting was just about to take place was determined by analysis. As with the analysis of the mixture at the point of maximum rate, the exact moment for the removal of the bucket from the furnace could not be accurately foretold. The bucket was weighed before and after the decomposition, and the loss in weight found. In one case, the weight loss was determined directly from the contraction in the spring, but this method was not favoured, for if there were an immediate loss in weight when the bucket was lowered into the furnace this would not be recorded. This occurred because the bucket and spring took about two minutes to become steady after the bucket had been lowered into the furnace. The " zero " reading of the cathetometer was thus taken 2·5 minutes after lowering the bucket. This also allowed the sample to reach the temperature of the furnace. The results (see table) show reasonable agreement :

Sample	Wt. loss = wt. of O_2, g.	Wt. of residue, g.		Wt., g.	Wt., %	Mol., %
C (0·1005 g.)	0·0056	0·0949	KCl	0·0061	6·43	11·0
			$KClO_3$	0·0031	3·27	3·5
			$KClO_4$	0·0857	90·3	85·5
V (0·1000 g.)	0·0062	0·0938	KCl	0·0061	6·5	11·3
			$KClO_3$	0·0073	7·8	8·2
			$KClO_4$	0·0804	85·7	80·5
T (0·1000 g.)	0·0067	0·0935	KCl	0·0067	7·2	12·5
			$KClO_3$	0·0054	5·8	6·0
			$KClO_4$	0·0814	87·0	81·5

The three runs were carried out at 530°. Nitrogen pressure in the reaction vessel was 5·2 cm. for V and T, and 2·6 cm. for C.

The residue was dissolved in water and the chloride estimated gravimetrically as silver salt. When the chloride was known, the chlorate content could be calculated from a knowledge of the weight of oxygen liberated.

Some of the runs indicated that the rate of loss of weight was constant for the initial part of the reaction but, as usual with this reaction, it was difficult to reproduce this effect.

DISCUSSION

The main difficulty observed during this reaction has been the variation of experimental results. In solid reactions, this is usually ascribed to differences in the nature of the surface of the crystals, or to various defects present in the interior of the crystals. In this reaction, however, these causes have little effect, as after a certain time the whole system becomes molten. It is, therefore, useless to try and apply theories and equations, which have been derived for chemical reactions involving solid decompositions, to explain the results of this decomposition.

Some measure of agreement for different runs was sometimes observed in the initial stages of the reaction, and it is suggested that a true solid decomposition is then taking place. When the reaction rate accelerates, this is due to melting of the reactants. The melt produced evolves oxygen quite rapidly, until towards the end of the reaction, when the amount of potassium chloride produced causes the mixture to solidify once more. The melting is associated with the formation of a eutectic mixture of chloride, chlorate, and perchlorate.

The process of the reaction is therefore : (*a*) Initial decomposition of solid perchlorate with formation of chlorate and chloride. The chloride produced will accelerate the reaction and melting takes place. This does not occur all at once, and it has been observed that some parts of the mixture are molten before other parts. The melting can be brought about in two ways : (i) Local inhomogeneities in the mixture may result in some portions having the composition of an approximately eutectic mixture of the three salts, which will melt at the reaction temperature. These areas will eventually coalesce to give a completely molten mixture. (ii) When the rate of production of chlorate from the perchlorate is greater than its rate of decomposition, it will accumulate in the mixture, and because of its low melting point, molten chlorate will be formed. The other salts will dissolve in this to form a molten mixture of the three salts.

(*b*) This stage is the decomposition of the melt, which has the appearance of a boiling viscous liquid owing to evolution of bubbles of oxygen. This bubbling causes spreading of the reaction mixture along the reaction tube. The composition of the melt will not therefore be constant, and we may thus expect variations in the rate of gas evolution with every sample, depending on how much ' splashing ' has taken place.

(*c*) Finally, the melt solidifies owing to the chloride ultimately formed, and the rate of gas evolution becomes slower.

The reaction cannot be represented by any one stoicheiometric equation, and probably the decomposition is the net result of several simultaneous reactions, the following being some of the possibilities : $2KClO_4 \longrightarrow 2KCl + 4O_2$, $2KClO_4 \longrightarrow 2KClO_3 + O_2$, $4KClO_3 \longrightarrow 3KClO_4 + KCl$, $2KClO_3 \longrightarrow KClO_4 + KCl + O_2$.

The small quantity of chlorine evolved probably arises from the chlorate produced. This was observed by Sodeau (*loc. cit.*). There has been much conjecture whether it is actually produced by the decomposing potassium chlorate, or by the action of one of the products of the reaction on some other product, or on the original material. We have been unable to obtain any definite evidence on this point. In this connection it is noteworthy that the residue was slightly alkaline, which may be associated with the presence of small amounts of potassium oxide.

The occurrence of the two peaks in the rate runs obtained by Glasner and Simchen (*loc. cit.*) may be explained by the catalytic influence of the potassium chloride contained in their material (up to 0·40%). The presence of a small amount of potassium chloride alters the whole course of the reaction. No double peaks were found in the rate curves with the pure material used in the present work, but they were found when the material was contaminated with chloride.

Since the above paper was written, two papers have appeared on similar topics. Glasner and Weidenfeld (*J. Amer. Chem. Soc.*, 1952, **74**, 2464, 2467) used purer material than previously (Glasner and Simchen, *loc. cit.*) and obtained results more in agreement with the foregoing. Their work was done at atmospheric pressure and gave only poor reproducibility.

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[*Received, July 24th,* 1952.]