XV.—*The Decomposition of Chlorates, with Special Reference to the Evolution of Chlorine and Oxygen. Part I.*

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THE ultimate object of this investigation is to ascertain the mechanism of the changes which take place when various chlorates are heated. These changes yield (in general) perchlorate, chloride, oxide, oxygen, and chlorine, but the relative proportions are known to vary very greatly with the nature of the base and with the mode of decomposition.

The present paper contains an account of experiments with barium chlorate and potassium chlorate, but other chlorates are being investigated, as also the mode of action of certain substances which facilitate decomposition. Throughout the paper, experiments are numbered in the order in which they were performed.

EXPERIMENTAL.

I. *Evolution of Chlorine from Barium Chlorate.*

"Pure" barium chlorate of commerce was found to be neutral and free from strontium and calcium, but contained traces of dust and of chloride; after separating barium with sulphuric acid, the filtrate left only a trace of residue on evaporation. The salt was purified by careful recrystallisation, drained on a perforated porcelain plate (to avoid fibres of paper), and dried at 135° after powdering. Barium chlorate, unlike the potassium salt, has but little tendency to creep or spirt when decomposed; some care is necessary in order to ensure its regular decomposition, as a rise of temperature may render the action violent, the mass becoming red hot. The influence of variations of temperature upon the rate of decomposition of the salt at atmospheric pressure has been investigated by Potilitzin (*J. Russ. Chem. Soc.*, 1887, [1], 339; *Ber.*, 1887, **20**, Ref. 769).

Mode of Decomposition at various Pressures.—A weighed quantity of the substance, usually 1 gram, was placed either in a soda-glass tube of 15 mm. bore closed at one end, or else in a platinum crucible contained in a closely fitting tube of about 28 mm. bore. The tube was then sealed on to a narrow one bent twice at right angles and ground into an absorption tube. When practicable, the gas was thus passed through pure potassium iodide solution (to which traces of iodine had been added until starch gave a faint coloration), and the liberated iodine was titrated with thiosulphate.* In the later experiments at 1 mm. pressure, the chlorine was retained by potassium iodide dissolved in glycerol and distributed over glass beads. It will be shown that the amount of free chlorine must be found by examination of the residue.

Two decomposition tubes and a thermometer were usually clamped side by side in a bath of melted pewter, one tube being at atmospheric pressure and the other connected to a Geissler mercury pump having a bulb of 630 c.c. capacity, the upper neck of this being calibrated, in order that the pump might be used as a McLeod gauge; the mercury manometer was only relied on when the pressure amounted to several mm. The evolved oxygen was always roughly measured by displacement of water in order to observe the progress of the decomposition. Before raising the temperature to the decomposition point, the last traces of water were removed by heating the chlorate to about 300° for some time, the tube was then twice exhausted, dry air free from carbon dioxide being admitted. It was not found practicable to

* The potassium iodide did not become alkaline; there was thus no evidence of the formation of ozone or of oxides of chlorine.

employ a constant temperature, for in order to avoid violent action at the commencement and yet complete the decomposition in the course of a few hours, it was necessary to gradually raise the temperature of the bath through 70° or more. The decompositions under reduced pressure took place, in general, at lower temperatures than those at atmospheric pressure, as equality in temperature would have necessitated a great difference in the duration of the experiment, owing to the marked manner in which reduction of pressure facilitates the decomposition, as shown in section III.

Absorption of small amounts of Chlorine by Heated Glass.—This was discovered by comparing the results of a few decompositions at 10—15 mm. with those at atmospheric pressure. Each decomposition lasted about two hours, and afterwards the residue and the contents of the absorption tube were titrated with hydrochloric acid and thiosulphate respectively. The original substance was perfectly neutral, and the standard solutions had been compared with each other by means of iodide and iodate of potassium.

Whether the substance was in a platinum crucible or placed directly in the tube, the amount of oxide in the residue, that is, its alkalinity, was but little influenced by the pressure, hence about the same amount of chlorine is *evolved* at 10—15 mm. and at atmospheric pressure. At 10—15 mm., the amount of chlorine reaching the potassium iodide was rather less than that lost by the residue, but at atmospheric pressure the contents of the absorption tube indicated no free chlorine, although sensitive to 1 drop $N/1000$ iodine; on the other hand, the residue neutralised, for example, 6 c.c. of $N/1000$ acid. It is thus evident that the chlorine had been absorbed by the heated glass. This absorption is lessened by reduction of pressure, or by passing a current of air, free from moisture and carbon dioxide, through the tube; treatment of the glass with steam is not an effective remedy.

Examination of the Residues.—Some experiments were conducted in order to ascertain the best method for titrating the oxide in the residue, this appearing to be the only reliable measure of the chlorine evolved. Phenolphthalein in the cold was found to be the most suitable indicator, as the large amount of barium chloride prevented the utilisation of the reaction between a slight excess of acid and a mixture of iodate (the iodine) and iodide of potassium to be titrated. As the total alkalinity is extremely small, it is important to avoid unnecessary dilution and to carefully guard against the presence of carbon dioxide. All the water used was boiled in a vacuum, and after this treatment 10 c.c. gave a pink coloration with phenolphthalein and 0·1 c.c. of $N/1000$ baryta; the burettes were provided with guard tubes containing soda lime. Decinormal hydrochloric acid was diluted to $N/500$ as required for use, the dilute baryta being titrated against this in the cold and then boiled with excess in order to ascertain the slight correction for carbonate present. In an estimation, the residue was dissolved in a slight excess of *N*/500 acid, boiled, quickly cooled in a desiccator containing soda-lime, and the excess of acid titrated with baryta; more acid was then added and the process repeated, in order to ensure the complete decomposition of any carbonate formed. This method was carefully tested and found to work well; owing to the dilution, there was no loss of acid on boiling nor were the titrations affected by addition of barium chloride or of neutralised barium peroxide.

To ascertain whether the presence of a trace of moisture during decomposition would introduce any considerable error, about 5 grams of finely powdered neutral barium chloride were introduced into a glass tube, a few drops of distilled water added, and the neck drawn out; this tube was placed in the bath during a slow decomposition (expt. 35) and the barium chloride heated in water vapour mixed with air for about 4 hours at 360—400° and then for 2 hours at 400—480° The alkalinity corresponded to the loss of only 0·035 per cent. of the chlorine present, so that the precautions adopted to remove moisture appear to have been more thorough than was really necessary, the effect being small in comparison with the amount producing it.

Portions of several residues were examined for barium peroxide by adding 1 c.c. of *N*/1000 permanganate to the solid, then a sufficiency of *N*/100 hydrochloric acid, and some potassium iodide. On titrating the liquid with thiosulphate, the volume required was usually rather less than in blank experiments, but the difference was too small to afford satisfactory evidence of the presence of barium peroxide; the proportion in the final residue must therefore be exceedingly small; this may, perhaps, be accounted for by the high temperature at the end of the decomposition.

Decomposition of the Chlorate (see Table I).—Experiments made simultaneously in the same bath have been distinguished from each other by the letters *a*, *b*, and *c*. Those "in contact with platinum" took place in narrow platinum crucibles, each enclosed in a glass tube and covered with an overlapping split cone of platinum foil, the object of the cover being to prevent surface cooling and to retain any splashes; each crucible was used at atmospheric and reduced pressures alternately, in order to eliminate any possible difference between the pair. In 31*a*, some pieces of glass tube were placed in the crucible, but neither in this experiment nor in the decompositions in glass tubes was there any indication of action between the chlorate and glass.

It was necessary that the decompositions should last some hours when the pressure was to be kept at 1—2 mm. by means of the mercury pump. At this pressure, the substance decomposed so much more readily that the temperature was at no stage raised to the fusing point of the mixture then present; at higher pressures, the mass always fused.

Where the duration is given as 0·5 minute, the decomposition was of a violent character, the mass becoming red hot. In expt. 47, the substance was dropped little by little into the already heated crucible (without the cone); the temperature would not rise so high as in the experiments just referred to, so this comes between the two other classes of experiments at atmospheric pressure. In the rapid decompositions, the amount of chlorine reaching the potassium iodide was comparable with that lost by the residue.

This series of experiments indicates that the proportion of free chlorine increases with the temperature, but is probably not affected by variations of pressure, as some allowance has to be made for the accompanying change of temperature (see theoretical part).

Decomposition of a Mixture of Barium Chloride and Chlorate.—H. Schulze (*J. pr. Chem.*, 1880, [ii], **21**, 407) found that barium

TABLE I.—*Barium chlorate.*

No.	In contact with	Pressure.	Duration (minutes).	N/1000 HCl c.c. per gram.	Cl evolved (total = 100).	Mols. chloride / Mols. oxide.
29*c*	Glass	1 atmosphere	0·5	48·8	0·74	134
31*b*	Platinum	,,	0·5	41·3	0·63	158
46	,,	,,	0·5	49·2	0·75	132
47	,,	,,	*	32·8	0·50	199
33	Platinum	1—2 mm.	200	4·0	0·061	1640
34*a*	,,	2 mm.	230	4·9	0·074	1340
35*a*	,,	1 mm.	270	4·2	0·064	1560
29*a*	,,	10—15 mm.	140	5·0	0·076	1310
32*a*	Glass	10—15 mm.	345	4·7	0·073	1400
29*b*	Platinum	1 atmosphere	140	5·5	0·082	1190
34*b*	,,	,,	250	6·1	0·093	1080
35*b*	,,	,,	340	7·4	0·112	890
45	,,	,,	50	5·0	0·076	1310
31*a*	Pt. and glass	,,	90	7·3	0·111	902
44*b*	Glass	,,	120	6·0	0·091	1090
44*a*	Glass and $BaCl_2$	1 atmosphere	120	5·6	0·085	1170
42	Pt. and $BaCl_2$	,,	300	6·4	0·097	1030
43	,,	,,	180	4·7	0·073	1370

* Rapid decomposition in small portions.

chloride remained perfectly neutral when heated to redness in dry oxygen, but supposed it to be partly converted into oxide by "nascent oxygen" when heated with potassium chlorate; the latter conclusion is traversed at the end of section III. The employment of *barium* chlorate avoids the possibility of double decomposition.

Some recrystallised barium chloride was roughly dried, finely powdered, and then dried at 155—160°, still remaining neutral. Mixtures having the composition $Ba(ClO_3)_2 + 2BaCl_2$ were decomposed at atmospheric pressure in the same manner as the chlorate alone. It will be seen from Table I (p. 141) that the amounts of chlorine (or oxide) obtained from such mixtures agree with those obtained without added chloride, although the average amount of chloride present was then only one-fifth. It is thus evident that the added barium chloride was not attacked by the decomposing fused chlorate or by any of the products.

II. *Decomposition Products of Potassium Chlorate.*

Several chemists have shown that pure potassium chlorate yields no free chlorine when decomposed in a platinum vessel under atmospheric pressure. On the other hand, Williams has stated (Proc., 1889, 5, 26) that the theoretical amount of oxygen was not obtained by heating the chlorate in a vacuum, that a gas, presumably chlorine, was given off which attacked mercury, and that the residue, therefore, probably contained peroxide.

The potassium chlorate used for the present work was obtained by repeated recrystallisation of the "pure" salt of commerce; special precautions were taken to avoid dust, &c., and the substance was finally dried at 115° after powdering. All the experiments with the substance in contact with glass were made before barium chlorate had been studied. Preliminary experiments indicated the absence of any considerable evolution of chlorine even when the pressure was reduced to a small fraction of a millimetre.

Decomposition with Chlorate in contact with Glass.—Portions weighing from 1 to 1·5 grams were decomposed in tubes of soda glass, Bohemian (combustion) glass, and Jena glass; the arrangement resembled that used for barium chlorate, but the tubes were heated either by radiation from an empty crucible or directly by means of a Bunsen burner provided with a chimney. The decompositions took place one at a time, and the results are given in Table II (p. 144).

In all these experiments, the amounts of free chlorine were very small. Before the decomposition of barium chlorate had been investigated, it was thought that the differences in experiments 19—22 indicated an evolution of chlorine under reduced pressure;

they are now regarded as showing that, at atmospheric pressure, the heated glass absorbs about 90 per cent. of the chlorine liberated by the action of the glass. The reabsorption of chlorine would (*cœteris paribus*) vary with the time of contact multiplied by the pressure (concentration) of the gas; this factor is given in the fifth column of Table II.

The amount of chlorine evolved seems to vary with the nature of the glass and with the mode of heating; the largest amount is obtained with Jena glass, its highly silicated nature probably causing a greater expulsion of chlorine and less reabsorption. It will be noticed that the heat of a flame seems to give rise to more action on the glass than the more evenly distributed radiation from a crucible; in either case, the greater part of the chlorine was evolved towards the end of the decomposition, when the temperature was sufficient to soften soda glass.

It has been repeatedly shown that potassium chlorate yields no free chlorine when decomposed at atmospheric pressure, yet in this series the largest amount was obtained in experiment 14; it is thus clear that the experiments of this series lead to fallacious results as regards the evolution of chlorine in the decomposition of the chlorate.

Decomposition in Platinum.—Except as indicated, the apparatus was identical with that used for barium chlorate. In the first pair of decompositions, the substance was decomposed in two narrow platinum crucibles each enclosed in a tube of Jena glass, one being kept at 10—15 mm. and the other at atmospheric pressure. The residues in the crucibles were neutral to phenolphthalein, but in each case some of the substance had reached the glass; this will account for the gas liberating a trace of iodine from the potassium iodide solution. On account of the tendency for potassium chlorate to creep and spirt, this series was not completed until after barium chlorate had been investigated and the best conditions ascertained.

In the final two pairs of decompositions, 40 and 41, each crucible contained 1 gram of potassium chlorate, and was covered with a piece of platinum foil bent round so as to form an inverted cone. The bath was kept at just over 400° for half an hour to drive off the last traces of moisture, and the tubes were then twice exhausted to 4 mm., dry air being admitted. The residues gave no pink colour with phenolphthalein even after boiling and cooling. A similar volume of water gave a very distinct pink with phenolphthalein and 0·1 c.c. of $N/500$ sodium carbonate, corresponding to 0·007 milligram of chlorine or 0·002 per 100 parts present. If, therefore, chlorine is evolved either at atmospheric pressure or at 1 mm., the amount cannot exceed this proportion. Determinations of free chlorine are evidently fallacious when the substance comes in contact with glass.

TABLE II.—*Potassium chlorate.*

No.	In contact with	Pressure.	Duration (minutes).	Duration × pressure.	Mode of heating.	N/1000 $Na_2S_2O_3$ c.c. per gram.	Cl *obtained* per 100 parts present.
13	Jena glass	10—15 mm.	120	1·9	Flame	1·4	0·017
14	,,	1 atmosphere	35	35	,,	6·0	0·074
23	,,	,,	50	50	Crucible	0·5	0·006
15	Soda glass	,,	10	10	Flame	0·6	0·007
18	,,	,,	25	25	Crucible	0·12	0·0014
16	Bohemian	,,	12	12	Flame	0·4	0·0047
22	,,	,,	100	100	Crucible	0·15	0·0018
19	,,	10—15 mm.	100	1·6	,,	1·6	0·019
20	,,	,,	150	2·4	,,	1·2	0·015
21	,,	,,	150	2·4	,,	1·3	0·016
40*a*	Platinum	1—2 mm.	240	0·5	Melted pewter		Much less than 0·002 *liberated*
41*a*	,,	1 mm.	330	0·4			
40*b*	,,	1 atmosphere	240	240			
41*b*	,,	,,	330	330			

When either Bohemian combustion or soda glass was used, the first half of the gas contained only an infinitesimal amount of chlorine.

III. *Experiments connected with the Rate of Decomposition.*

The mode of working was similar to that described on p. 138, potassium nitrate being occasionally substituted for metal in the bath on account of its transparency. The evolved oxygen was measured by displacement of water, or by collection over water in a graduated tube; in most experiments, the loss of weight was also determined.

Potassium Chlorate under Reduced Pressure.—Veley (*Phil. Trans.*, 1888, Pt. I. 282) has shown that the early stages of the decomposition are not influenced by reduction of the pressure to 20 mm., and the experiments described in section II appeared to indicate that variations of pressure had no influence upon the rate at any stage of the decomposition. This was more exactly proved by decomposing equal weights in a pair of similar bulbs, and, although one was at 1 mm. and the other at atmospheric pressure, the volumes of oxygen evolved from either agreed as well as could be expected during the whole of the six hours required for complete decomposition. This would seem to indicate that the formation of perchlorate is not greatly affected by variation of pressure, as otherwise a marked difference would be expected in the latter part of the decomposition.

Barium Chlorate under Reduced Pressure.—In this case, the previous experiments (section I) had indicated a very considerable facilitation in the evolution of oxygen, resulting from reduction of pressure. This has been confirmed by decomposing equal weights in paired bulbs. The temperature was kept fairly uniform during the first part of the decomposition, but was afterwards raised; readings were taken every five minutes. The general character of the results is indicated in the table.

Time.	O evolved (total = 100).		Time.	O evolved (total = 100).	
	At 1 atm.	10—15 mm.		At 1 atm.	1 mm.
45 mins.	6·2	22·2	80 mins.	1·6	24·7
60 ,,	13·6	41·5	140 ,,	4·7	37·7
75 ,,	22·9	55·7	200 ,,	10·1	41·9
90 ,,	31·7	59·2	260 ,,	20·2	45·6
160 ,,	49·1	60·5	320 ,,	39·9	49·1
315 ,,	67·5	85·5	400 ,,	43·7	52·6
			490 ,,	45·9	70·3

In the experiment recorded to the left, the temperature of the bath was about 380° (corr.) during the first 160 minutes; decomposition was practically complete (31·6 per cent. oxygen) after 400 minutes at atmospheric pressure, or 345 minutes at 10—15 mm. In neither experiment was there any *definite* break in the decomposition; further work will therefore be required in order to ascertain the influence of variation of pressure upon the proportion of perchlorate.

Effect of Barium Chloride on the Decomposition of Barium Chlorate.—The experiments described in the latter part of section I had shown that the presence of the chloride caused a marked retardation, as the temperatures of the bath had been higher than when barium chlorate was decomposed alone. The following table gives examples of the proportions of oxygen evolved during the decomposition of equal weights of barium chlorate alone and mixed with two molecular proportions of the chloride. Paired glass bulbs were used, and the total oxygen taken as 100.

Minutes.	30.	40.	50.	60.	65.	70.	85.	100.	110.	120.
$Ba(ClO_3)_2$	9·0	25·4	38·6	45·9	50·7	51·6	56·6	73·8	95·9	100
$Ba(ClO_3)_2 + 2BaCl_2$ ...	4·9	6·6	10·7	13·2	26·2	50·0	52·5	70·5	96·7	100

The temperature of the bath was progressively raised; during the first part of the decomposition, the mixture did not reach a given stage until the temperature was about 20° higher than when the pure chlorate attained the same degree of decomposition. It will be noticed that the chloride had very little effect after about half the oxygen had been evolved; a fair amount of chloride had then been formed by decomposition, and the temperature was much higher. Facilitation by reduced pressure and retardation by the addition of chloride may perhaps indicate an inverse action.

Effect of Potassium Chloride on the Decomposition of Potassium Chlorate.—The two specimens of chloride used in these experiments were each prepared by decomposing some of the chlorate in a platinum crucible heated by a spirit flame. Equal weights of potassium chlorate, with and without addition of chloride, were decomposed in similar tubes the volume of oxygen was noted at intervals of 1 to 2 minutes. A very slight *facilitation* was observed; taking the average of four pairs of decompositions, about one-third more oxygen was evolved in a given time when one molecular proportion of chloride had been added.

Action of Heat on a Mixture of Potassium Chlorate and Barium Chloride.—In this series of experiments, potassium chlorate and mixtures having the composition represented by $2KClO_3 + BaCl_2$ and $Ba(ClO_3)_2 + 2BaCl_2$ were heated in similar tubes, the quantities employed containing equal amounts of oxygen.

In comparing potassium chlorate with the mixture $2KClO_3 + BaCl_2$, the latter lost 59·1 per cent. of its oxygen in 35 minutes, but only 3·1 per cent. had been evolved from the pure chlorate; in another experiment, the mixture lost 10·7 per cent. of its oxygen with more gentle heating for 45 minutes, but the pure chlorate had then undergone no appreciable loss. Except in the early stages, the temperature required to produce a given rate of decomposition in this mixture is more or less comparable with that required for the mixture $Ba(ClO_3)_2 + 2BaCl_2$, and about 50—60° lower than with potassium chlorate alone, although potassium chloride has but little effect and barium chloride markedly *retards* the decomposition of barium chlorate.

Fused barium chlorate has but little solvent action upon barium chloride, but potassium chlorate readily "dissolves" half an equivalent of it; hence, when the mixture $BaCl_2 + 2KClO_3$ is heated, about half the barium chloride at once goes into solution. Under these circumstances, double decomposition must occur to a greater or less extent, and the ease with which the mixture is decomposed points to the continuous formation of barium chlorate, from which the oxygen is derived.

THEORETICAL.

The proportion of chlorine liberated during the decomposition of chlorates by heat depends mainly on the nature of the base and the mode of heating. In order to explain this, two theories have been suggested. Schulze (*loc. cit.*) supposed the chlorate to decompose entirely into chloride and oxygen, the chlorine resulting from the action of "nascent oxygen" upon the chloride. W. Spring and Prost (*Bull. Soc. Chim.*, 1889, [iii], 1, 340), on the contrary, suggested that the chlorate decomposes entirely into oxide and chloric anhydride, Cl_2O_5, the latter immediately breaking up into chlorine and oxygen, more or less of the chlorine then reacting with the oxide to form chloride with the liberation of more oxygen.

It will be noticed that these explanations are in direct opposition, but in neither of the papers does there appear to be evidence that the suggested second action actually takes place under the conditions obtaining in the decomposition, nor does either deal with possible alternatives, of which there would seem to be two, namely, (1) the simultaneous formation of both oxide and chloride as *direct* products and (2) the simultaneous action of chlorine and oxygen upon the residue first produced.

For the purpose of discussion, it is convenient to classify the different reactions which might give rise to the formation of oxide and chloride (evolution of chlorine and oxygen) during a decomposition.

(*a*) Chlorate giving chloride and oxygen.

(*b*) Chlorate giving oxide, chlorine, and oxygen.

(*c*) Chlorate acting upon chloride with liberation of chlorine.

(*d*) Oxygen and chloride giving chlorine and oxide, apart from reverse action (*e*).

(*e*) Chlorine and oxide giving oxygen and chloride, apart from reverse action (*d*).

(*f*) Simultaneous action of oxygen and chlorine, as in (*d*) and (*e*) combined.

Decomposition of Barium Chlorate.—Averaging three of the series of experiments given in Table I, we obtain the following:

Pressure.	Duration (minutes).	Duration × Pressure.	Total Cl = 100		$\frac{\text{Mols. chloride}}{\text{Mols. oxide}}$
			Free Cl.	Cl as chloride (by difference).	
1—2 mm.	233	0·5	0·066	99·934	1513
1 atmosphere	165	165	0·093	99·907	1077
,,	0·5	0·5	0·704	99·296	141

The action between a gas and a solid is usually increased by rise of temperature, and increases with the time of contact and the concentration of the gas; the two latter factors are included in the numbers given in the third column (duration multiplied by pressure in atmospheres). According to Spring and Prost, the chloride is produced by the action of chlorine upon the oxide first formed. Comparing the slow decompositions at 1—2 mm. and at 1 atm., we find that a slight fall of temperature combined with a reduction of the time-concentration factor from 165 to 0·5 has very slightly *increased* the amount of chloride from 99·907 to 99·934 per cent. of the possible amount, instead of very greatly decreasing it. Hence the chloride must be formed in another way, and Spring and Prost's theory does not hold for this chlorate.

Any reabsorption of chlorine which occurs is evidently not complete at atmospheric pressure, and would be much less so when the concentration of the gas is reduced by expansion (compare the experiments proving reabsorption by heated glass); such reabsorption therefore necessitates an increase of free chlorine on reduction of pressure, but none occurs at 1—2 mm., hence reaction (*e*) cannot occur to an appreciable extent. It may be noted that both oxide and chlorine are very greatly diluted with chloride and oxygen respectively. Comparing the effect of rapid decomposition at atmospheric pressure with that of reduction of pressure to 1—2 mm., we see that in either case the time-concentration factor has been reduced to about 0·5, yet this change has been accompanied by a slight *decrease* of chlorine in the latter case, but by a sevenfold *increase* in the former. The increase with rapid decomposition must therefore be due to the great rise of temperature instead of to rapidity of removal of the gaseous products as supposed by Spring and Prost. The increase does not really seem a necessary consequence of this theory, as the rapid formation of oxide would partly compensate for the decrease in the time, and the great rise of temperature might even cause more complete absorption by accelerating the reaction between oxide and chlorine. It seems probable that the proportion of free chlorine is not affected by variations of pressure and that the slight decrease at 1—2 mm. is due to reduction of temperature.

Schulze's hypothesis cannot apply to barium chlorate, for it has been shown that no chlorine is expelled from barium chloride by barium chlorate or any of its decomposition products under the conditions actually obtaining during a decomposition. It has also been noticed that the first bubbles of gas contained about the average proportion of chlorine, although only traces of chloride had then been formed. The chloride experiments exclude reactions (*c*) and (*d*), and show that, in this case, (*f*) coincides with (*e*), which has also been excluded; as chloride and oxide are actually formed, it is concluded that reactions (*a*) and (*b*) occur during the decomposition, the average velocity of (*a*) being about 1000 to 1500 times that of (*b*) when the decomposition proceeds slowly, but at a higher temperature, when the decomposition is rapid, the ratio is only about 140 : 1. These average velocities represent the number of molecules of chloride to each molecule of oxide.

From the heats of formation, we obtain :

$$(a) \quad 2Ba(ClO_3)_2 \quad 2BaCl_2 + 6O_2 + 438K.$$

$$(b) \begin{cases} 2Ba(ClO_3)_2 = 2BaO + 2Cl_2 + 5O_2 - 972K. \\ 2Ba(ClO_3)_2 = 2BaO_2 + 2Cl_2 + 4O_2 - 624K. \end{cases}$$

The result of rapid decomposition thus appears to be merely an example of an endothermic reaction (*b*) gaining upon an exothermic one (*a*) when the temperature is increased.

Decomposition of Potassium Chlorate.—In this case, the evidence is of a somewhat negative character, but as less than 0·007 milligram of chlorine is present in the 400 litres of gas (measured at about 530° and 1·5 mm.) from 1 gram of the substance, it seems extremely improbable that any appreciable amount is evolved at first. The last stages of the reabsorption would be exceedingly slow, as the oxide would then have been all but completely transformed into chloride; in the final residue, less than 0·002 per cent. of the potassium can remain as oxide. The improbability is increased by the fact that no such reabsorption was detected in the decomposition of barium chlorate at atmospheric pressure when the proportions of oxide and of free chlorine were respectively at least 50 times and 25,000 times those just given for potassium chlorate.

It appears that the direct decomposition into chloride and oxygen is the only one which need be considered, this proceeding at a rate at least 50,000 times as great as any reaction yielding chlorine.

General Considerations.

The experiments in this paper, and some already performed with lead chlorate and calcium chlorate but not yet published, tend to indicate the general conclusion that when a chlorate is heated it undergoes two simultaneous and independent decompositions, (*a*) into chloride and oxygen, (*b*) into oxide, chlorine, and oxygen ; it remains to be shown that this view will harmonise with the results of Schulze's and of Spring and Prost's experiments. In each of these papers, a point is made of the increase of chlorine with increase of weakness of the base ; now as the affinity for oxygen approaches that for chlorine, there would be more tendency for oxygen to attack the chloride, less for chlorine to react with the oxide, and more tendency for the oxide to be directly produced ; this point therefore accords equally with each of the three theories. The increase of chlorine with rapid decomposition has already been dealt with under barium chlorate; the only remaining point brought forward by Spring and Prost is the suggestion that the proportion of free chlorine is increased by addition of an acidic oxide because it combines with the liberated basic oxide and so prevents reabsorption of the chlorine first liberated. This cannot, however, be a generally correct explanation, for many such substances cause this action with potassium chlorate when 50—200° below the temperature at which this salt undergoes appreciable decomposition when heated alone (Baudrimont, *J. Pharm.*, 1871, [iv], **14**, 81 and 161; Fowler and Grant, Trans., 1890, **57**, 272); the "liberated oxide" would then be non-existent. It does not seem remarkable that these substances should expel chlorine and oxygen (chloric anhydride) from chlorates, as many expel sulphuric anhydride from sulphates.

Schulze also shows that the amounts of free chlorine obtained by the decomposition of the chlorates of sodium, barium, and strontium agree with those resulting when equivalents of the chlorides are heated with potassium chlorate, and that comparable results would probably be obtained with other metals. Double decomposition, however, would be expected to take place with the formation of a chlorate more readily decomposed than that of potassium; these experiments would thus be decompositions of the respective chlorates rather than a study of the action of "nascent oxygen." In section III this has been shown to be the case with barium chloride, and there seems little doubt that the same will apply with other metals, as reaction takes place at a relatively low temperature.

It thus appears that the theory of two independent decompositions is in harmony, not only with the present investigation, but also with the results supposed to support the two older theories.

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