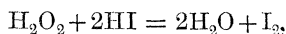


"An Investigation of a Case of Gradual Chemical Change: the Interaction of Hydrogen Chloride and Chlorate in presence of Potassium Iodide." By W. H. PENDLEBURY, B.A., late Scholar of Christ Church, Oxford, Assistant Master of Dover College, and MARGARET SEWARD, late Tutor of Somerville Hall, Oxford, Science Lecturer of Holloway College. Communicated by A. VERNON HARCOURT, F.R.S. Received November 27,—Read December 13, 1888.

The work which we now have the honour of laying before the Royal Society was undertaken at the suggestion of Mr. A. Vernon Harcourt. To him we owe more than we can express, and we desire here to thank him most heartily for his most valuable aid and co-operation, by which many rough places in the investigation have been made smooth. We also thank the Royal Society for a grant in aid of the research, and the Governing Body of Christ Church for the use of materials and apparatus.

When substances which act upon each other are brought together under suitable conditions, a change takes place which consists in the disappearance of the original substances and the production in their place of an equal weight of other substances. The change proceeds till the whole of that reacting substance which was present in the smallest relative quantity has disappeared. This process may take a long time, as in the case which forms the subject of the present investigation, or the limit may be reached so rapidly that the change seems instantaneous. This difference, however, is one of degree and not of kind. In the present case the masses of the substances mixed together were so large relatively to the masses undergoing change during the time over which the observations extended, that the masses of reacting substances were practically constant. Thus it happens that each set of observations was of a change proceeding with constant velocity. In the second reaction studied by Messrs. Harcourt and Esson—



the amount of change occurring during each interval of time in which it was estimated was a considerable fraction of the total amount of potential change, as limited by the amount of hydrogen dioxide taken. In this case, therefore, the observed intervals of time lengthened, being the time required for the performance of the same amount of chemical work with a continually diminishing amount of active substance.

The measurement of these intervals of time (whether constant or increasing) during which the same amount of chemical decomposition takes place, can be effected by taking advantage of a comparatively instantaneous change which may be made to go on in the same liquid, and one which is very familiar.

When iodine is produced in a liquid by the action of hydrogen dioxide, or some other oxidising agent, on hydrogen iodide, the action is a gradual one, but the introduction of a drop of a concentrated solution of sodium thiosulphate at once converts the iodine into sodium iodide, and every molecule of iodine produced in the liquid after the introduction of the drop will be instantly thus converted until the thiosulphate present is exhausted. If a small quantity of starch is present in the solution, the moment at which the last trace of thiosulphate disappears will be signalled by the appearance of a blue colour in the liquid, the effect of the free iodine upon the starch. Thus, then, by the introduction of constant measured quantities of sodium thiosulphate, the rate of progress of the action between potassium or hydrogen iodide and some oxidising substance may be readily measured. This is the principle and method of division into intervals in Messrs. Harcourt and Esson's classical research, and we have adopted it for the investigation of a similar case of chemical change.

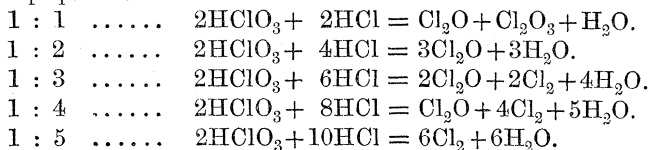
The reaction chosen for investigation in the present case was one which liberated iodine indirectly. When solutions of potassium chlorate and hydrogen chloride are mixed together, the mixture soon acquires a chlorous smell, and at once liberates iodine from potassium iodide, and as time goes on continues to liberate more. The exact nature of the primary reaction, producing the oxidising agent, has not been ascertained, nor whether the product is chlorine, some oxide of chlorine, or a mixture of both. Various reactions are possible. The one fact which is certain seems to be that in presence of an iodide each molecule of chlorate salt is reduced to the corresponding chloride entirely and without intermediate stages, and the equivalent in iodine of all three atoms of oxygen set free. If it were the case that the decomposition of the chlorate molecule took place in stages there would be observed a considerable variation in the intervals depending on the amount of intermediate products present, which was not the case.

A mixture of hydrogen chlorate and hydrogen chloride, both dilute, reacts exactly in the same way as the mixture above, slowly producing oxidising material which liberates iodine from potassium iodide. It is probably a reaction common to most soluble chlorates. Part of the investigation has been concerned with such mixtures of the two acids without any metallic salt. These have advantages, as the reaction is not complicated by the presence of such salts. But

potassium chlorate was more often employed, being easily obtained and kept in a state of purity.

Bunsen gives the following hypothetical equations for a reaction between hydrogen chloride and any chlorate (the equations are given with hydrogen chlorate, for simplicity). But in these the number of molecules of chlorate reacting is arbitrarily limited to two. Without this limitation, it is obvious that the list of possible reactions may be indefinitely extended.

Relative proportion.



In our experiments the quantity of reacting substances was always such that, except for change in sodium thiosulphate, the composition of the mixture was sensibly the same at the end of the experiment as at the beginning. Each experiment was not carried to any definite limit, but was concluded as soon as the constant velocity of change in the mixture had been ascertained by the observation of several intervals corresponding to successive additions of thiosulphate.

The following considerations show the constancy of the composition of the mixture throughout an experiment. Each drop of thio-sulphate corresponded, on an average, to the decomposition of three-millionths of a gram of potassium chlorate in each cubic centimetre of the mixture. Now, the smallest amount of potassium chlorate ever used was 0.01263 gram in each cubic centimetre, and of this only 0.000003 gram would have disappeared when as many as 10 drops of sodium thiosulphate had been added. This is an alteration of about 0.02 per cent. Or, to state it otherwise, in the case of one of the greatest velocities observed, when each interval was hardly greater than a minute, there was 0.03788 gram potassium chlorate in each cubic centimetre, and this was disappearing at the rate of 1.826-millionths of a gram per minute. Speaking roughly, it would take about 24 hours, proceeding at this rate, to cause a difference of 1 per cent. in the amount of salt present.

Messrs. Harcourt and Esson represented the variation of the intervals they observed with the mass present,  $y$ , as a logarithmic curve with asymptote meeting it when  $y = \infty$ . The constant intervals obtained in the present investigation would be represented in a portion of the curve produced to a great distance in the direction of the asymptote, this portion being sensibly a straight line parallel to the asymptote, so that the time observed for each interval is constant.

In our ordinary mode of working the reaction between chlorate and chloride occurred in presence of iodide. In order to examine the reaction when only chlorate and chloride were present and the products of their reaction were not at once reduced, and thus removed, the following experiments were made. Through a vessel containing a mixture of hydrogen chloride and potassium chlorate, kept at a constant temperature of  $30^{\circ}$ , a certain volume of air could be drawn at a fixed rate. The air, thus charged with a part of whatever gas was liberated in the mixture, was drawn through a series of washing-tubes containing potassium iodide. The liberated iodine was determined at the end of equal intervals of time. It was found that comparatively little oxidising gas was evolved. At the end of 20 hours the amount of gas dissolved in the mixture, capable of liberating iodine, was determined, and this quantity also was found to be very small. The remarkable diminution in the rate of formation of oxidising substance when no iodide was present will be evident when it is stated that whereas, in the presence of iodide, the change proceeded at such a rate that in 20 hours the amount of iodine set free would have corresponded to 6700 c.c. of the standard thiosulphate, the oxidising material formed in absence of an iodide only set free iodine corresponding to 100 c.c. thiosulphate.

The action was also found to be reversible in sunlight. Some of the mixture of potassium chlorate and hydrogen chloride, which had acquired a deep yellow colour, was exposed for a short time to bright sunlight; the solution became colourless, and was found to liberate no iodine. In our experiments, in presence of an iodide, we found sunlight to have no effect upon the rate of change.

It would thus appear that when the oxidising substance is produced in presence of an iodide it does its oxidising work at once and is removed, and the change proceeds uniformly. In the absence of an iodide, however, the oxidising substance accumulates in the liquid, and its further production is impeded probably by the occurrence of a reverse action.

Though the potassium iodide appears thus to be a necessary ingredient of the mixture if the change is to proceed at a uniform rate, it does not take part in the primary reaction; for otherwise variation in the amount of potassium iodide in the mixture, other things being unaltered, would produce very marked differences in the rate. That this is not the case was proved by an experiment, the results of which are shown in the following table:—

Table A.

<i>n.</i>	R.	<i>n.</i>	R.	<i>n.</i>	R.
1	61·30	5	66·18	9	65·98
2	63·20	6	65·93	10	65·93
3	64·42	7	66·10	11	66·16
4	65·50	8	66·40	12	66·73

In this table are given the rates, representing the number of hundred millionths of a gram of potassium chlorate decomposed per minute in each cubic centimetre of the liquid. The mixture contained in each cubic centimetre

$$\begin{cases} 0\cdot03789 \text{ gram potassium chlorate.} \\ 0\cdot02496 \text{ gram hydrogen chloride.} \end{cases}$$

The potassium iodide present during successive intensities was  $n \times 0\cdot000001978$  gram, and  $n$  varied from 1 to 12.

It will be noticed that there is at first a slight acceleration with increase of potassium iodide, but very far from proportional to the increase, as would be the case if the reaction depended primarily on the amount of iodide present. After  $n = 5$  the further multiplication of the small quantity produced little if any change in the rate. Perhaps the minute amount of iodide present during the first few observations was insufficient for the immediate amount of the chlorine and chlorous oxides formed.

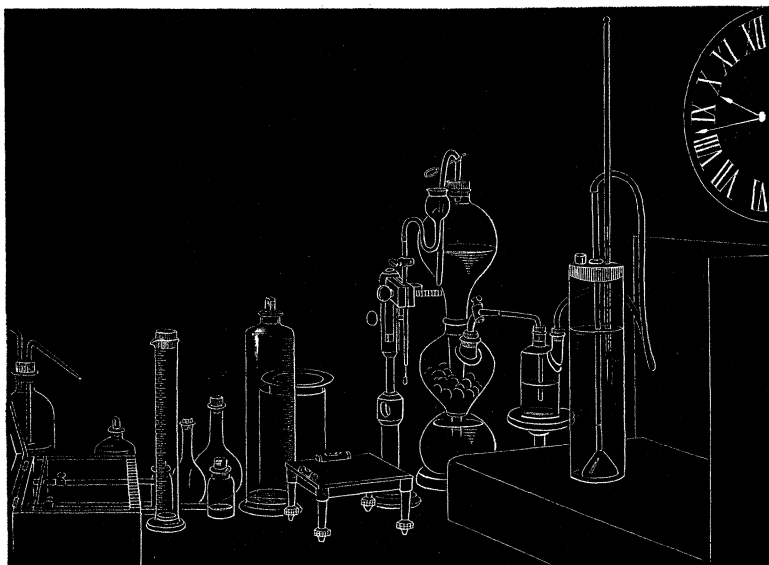
In fact the above numbers, besides showing that the liberation of iodine is a separate reaction, not the primary one, seem also to indicate that though with the quantity of potassium iodide usually taken this secondary reaction *is* instantaneous compared with the primary one, if the quantity is much decreased the former does take up a time which is comparable with that of the latter, and so may produce an appreciable retardation.

We shall return to the consideration of variation of potassium iodide later on, but have pointed this out to emphasise further the observation already made, that time must be a factor in all changes, but in very few does the connexion come within our powers of observation, so that other changes compared with these few are called instantaneous.

The amount of potassium iodide generally used in our experiments corresponds to  $n = 60$  in this series. In other sets of observations some of which are recorded in Tables XI, XII, and XIII, p. 417—419, the effect of adding larger amounts of potassium iodide was tried. The

effect is to produce a slight addition to the rate, proportional to the amount of iodide added. A similar result has been obtained with potassium chloride, and in view of these results we conclude that potassium iodide acts only as an indifferent salt, and does not immediately promote the reduction of the potassium chlorate, but only serves to prevent the accumulation in the liquid of chlorine or chlorine oxides precisely as the presence of thiosulphate serves to prevent the accumulation of iodine.

FIG. 1.



The apparatus employed in all our experiments was the same as that used by Messrs. Harcourt and Esson, and consisted of a cylinder of white glass 310 mm. high and 64 mm. in diameter; at a distance of 213 mm. from the base a fine line was etched round the cylinder marking a volume of 792 c.c. The cylinder was closed with an india-rubber stopper perforated with three openings, through which passed a thermometer and an inverted funnel tube. The third hole was ordinarily closed with a cork, and served to give access to the contents of the cylinder. The inverted funnel tube was connected with an apparatus for the generation of carbon dioxide.

The method of proceeding was as follows:—Into the cylinder previously filled with carbon dioxide was brought the weighed quantity of potassium chlorate to be employed, with sufficient water to dissolve it. To this was added a measured volume of hydrogen chloride of

known strength, together with 10 c.c. of potassium iodide solution containing 0.1 gram of the salt and 10 c.c. of clear starch solution, mixture being rapidly made after each addition by the passage of large bubbles of carbon dioxide from the inverted funnel. These bubbles of gas, with a diameter equal to half that of the cylinder, served to stir the liquid and also to exclude the air. A few drops of a dilute solution of thiosulphate were added to keep down the blue colour till all was prepared for observation. There was a line scratched on the funnel stem, and this mark and one of the graduations of the thermometer were made to coincide with the plane of the line round the cylinder. The temperature of the liquid was brought up to the required point, then the cylinder was placed on a levelling stand, and water was added till the lower surface of the meniscus just coincided with the plane of the marked line. Meanwhile a number of small measures of a concentrated solution of sodium thiosulphate had been prepared. These measures must be equal or have a known ratio to each other; they must also be of small volume, in order that their addition may not materially affect the dilution of the liquid. These measures were obtained in the following way:—A series of tubes about 8 inches long, having a lateral orifice about  $1\frac{1}{2}$  inches from the end, such as would be made for the purpose of joining on another tube at right angles, were mounted on a carriage, each tube having a separate rest, and all the orifices being in one line. By the turn of a screw connected with a rack and pinion these tubes could be brought exactly under a siphon delivering drops of thiosulphate. The siphon and its reservoirs stood on a bracket attached to a pillar of solid masonry to prevent vibration. The whole was enclosed in a glass case like that of a balance, the front of which was shut down during the time of collection of the drops. The time of formation of a drop was generally about half a minute. The width of the reservoir containing the thiosulphate is so great in comparison with the quantity of solution taken for any one set of experiments that the available length of the siphon and the rate of flow, upon whose constancy that of the drops depends, varies in no appreciable degree. At the end of each experiment the value of the drops employed was determined by means of a standard iodine solution.

When the observations were to be made the cylinder was placed on a sheet of white paper in a good light, opposite a clock beating seconds. The paper lay on an iron plate, which could be heated at once, and by a lamp if necessary, and thus the cylinder could be kept at any desired temperature by moving it nearer to or further from the heated end of the plate. When once the most convenient spot has been selected, a mere touch with the hand was all that was required to maintain the temperature constant.

The observations were made by looking down on the column of fluid and watching the appearance of the disk forming its upper surface. As soon as the change is complete a blue shade shoots rapidly across the brightly illuminated disk, and there is no difficulty in ascertaining the exact second of the change; the observer listens to the beat of the clock and counts the seconds whilst watching the disk. As soon as the blue colour has appeared, the minute and second are noted, and a drop of thiosulphate is brought into the cylinder. The end of the tube charged with a drop is plunged into the liquid through the opening for that purpose, and moved up and down, active stirring being carried on by means of the bubbles of carbon dioxide. The intervals date from one appearance of the colour to the next reappearance, and as the rate is not affected by the presence of a small amount of iodine or a small diminution in the amount of iodide, it is clear that the fact of the addition and admixture of the thiosulphate not following immediately upon the appearance of the blue colour, does not disturb the uniformity of the rate of change.

The potassium chlorate employed in our experiments was purified by recrystallisation.

The hydrogen chlorate was prepared by the cautious addition of sulphuric acid to a solution of pure barium chlorate until no milkiness was produced either by further additions of hydrogen sulphate or barium chlorate. The barium sulphate precipitate was then filtered off. The solution of hydrogen chlorate thus obtained contained no chloride.

The potassium iodide solution was prepared by dissolving 80 grams of recrystallised and fused potassium iodide in 8 litres of water.

The starch solution employed was prepared by adding a magma of starch and water, containing about 5 grams of starch to about 300 c.c. of boiling water, and allowing the whole to boil briskly for a few minutes. When cool, the liquid was transferred to a cylinder and covered over. On standing, the upper part of the liquid become perfectly clear; of this 10 c.c. were taken by means of a pipette.

The hydrogen chloride solution was prepared by diluting pure acid till 100 c.c. contained 18.823 grams of hydrogen chloride.

It may be of interest here to give the details of an actual experiment.

Taken—30 grams of potassium chlorate, 200 c.c. hydrochloric acid (containing 18.823 grams hydrogen chloride in 100 c.c.), 10 c.c. of a clear starch solution, and 10 c.c. of a solution of potassium iodide (containing 0.01 gram potassium iodide per c.c.). A few drops of a dilute solution of thiosulphate were added to discharge the colour due to the iodine liberated before it was possible to commence observations.

The temperature throughout was 20°.



As soon as all was ready the time of the first reappearance of the blue colour was noted, then a drop of thiosulphate was introduced as described, and the next appearance of colour was noted.

Table B.

Time.	Interval.	
	Mins. secs.	Mins. and decimals of a min.
I 38 24	1 38	1.63
I 40 2	1 39	1.65
I 41 41	1 39	1.65
I 43 20	1 39	1.65
I 44 59	1 38	1.63
I 46 37	1 38	1.63
I 48 15	1 39	1.65
I 49 54		
		Mean 1.64

The value of each of the thiosulphate drops in standard iodine solution was then determined.

The equivalent of one drop is 6.05 c.c. of this solution, containing 0.00248 gram iodine per c.c. Now 1 millionth-gram-molecule of potassium chlorate liberates 7.62 millionth-grams in weight of iodine.

Therefore the number of millionth-gram-molecules of potassium chlorate decomposed in each cubic centimetre of the mixture per minute is

$$\frac{6.05 \times 0.00248}{7.62 \times 792 \times 1.64} = 0.01512 \text{ mgm.}$$

The quantities taken of the reacting substances represented

$$\begin{array}{ll} \text{HCl} & \dots\dots 20 \times 65.11 \text{ m.g.m. per c.c.} \\ \text{KClO}_3 & \dots\dots 30 \times 51.5 \quad \quad \quad \text{,,} \end{array}$$

#### *Scheme of the Paper.*

In describing the results of our investigations we shall first consider the action of hydrogen chlorate on hydrogen chloride and examine the effect of variation of the former acid on the rate of change; we next consider the effect of variation in hydrogen chloride on such a mixture. We then consider and examine the effect of introducing potassium chloride into the mixture of the two acids, and from the results thereby obtained we gain considerable help in our

further investigation, viz., the action of hydrogen chloride on potassium chlorate.

In this reaction we examine the effect on the rate of variation in the amount of hydrogen chloride, the potassium chlorate being kept constant. We then briefly touch on the results obtained by varying the potassium chlorate.

We next consider the effect of variation in the amount of potassium iodide present, used as an indicator of the performance of a definite amount of chemical work.

We lastly discuss the effect of variation in the temperature at which the reaction of hydrogen chloride and hydrogen chlorate takes place.

*Variation in Hydrogen Chlorate.*

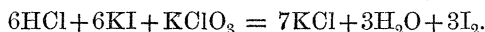
A series of observations were made in which the quantity of hydrogen chlorate was varied in arithmetical progression, the hydrogen chloride being kept constant. When each of the numbers representing velocity of decomposition was divided by a number representing the amount of hydrogen chlorate present, the series of numbers obtained was approximately an arithmetical progression, the difference being a small one. So that if  $u$  represents the hydrogen chlorate,  $R$  the rate of decomposition, a formula by which the latter may be calculated from the former is of the form

$$R = u(A + Bu),$$

where  $A$  and  $B$  are constants.

The following tables contain examples of the results obtained by experiment, and by calculation from this formula.

The rate = the number of times the following reaction in millionth of a gram-units takes place in each c.c. per minute.



$\text{HCl} = 16 \times 65 \cdot 11$  millionth-gram-molecules in each c.c.

$\text{HClO}_3 = u \times 61 \cdot 3$

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„

$u$  varies from 2 to 6.

Table I.

$u$ .	Rate observed.	Rate calculated. $R = u(0\cdot00073 + 0\cdot00025u)$
2	0·00246	0·00246
3	0·00434	0·00444
4	0·00695	0·00692
5	0·00996	0·00990
6	0·01320	0·01338

Table II.

$$\text{HCl} = 20 \times 65.11 \text{ m.g.m.}$$

$$\text{HClO}_3 = u \times 61.3 \text{ m.g.m.}$$

<i>u.</i>	Rate observed.	Rate calculated. $R = u(0.00244 + 0.00035u).$
2	0.00628	0.00628
3	0.01028	0.01047
4	0.01542	0.01536
5	0.02090	0.02095
6	0.02858	0.02724

Table III.

$$\text{HCl} = 15 \times 65.11 \text{ m.g.m.}$$

$$\text{HClO}_3 = u \times 61.3 \text{ m.g.m.}$$

<i>u.</i>	Rate observed.	Rate calculated. $R = u(0.00083 + 0.00016u).$
3	0.00393	0.00393
4	0.00578	0.00588
5	0.00800	0.00815
6	0.01074	0.01074

The connexion between the velocity of decomposition and the amount of the decomposing substances present is of exactly the same nature as that established in a similar way by Messrs. Harcourt and Esson, viz., that the velocity varies in the first place directly with the mass of the substance present, and that in the second place the presence of the substance causes a slight acceleration in the rate irrespective of its being decomposed. It has already been conclusively shown by their work and that of other experimenters on the same lines that the presence in the liquid of any substance which, as far as is known, has no chemical action upon the essential ingredients, and may therefore be considered to remain inactive during the change nevertheless has its specific effect, accelerating or retarding upon the velocity of the change. But Harcourt and Esson pointed out that the decomposing substance itself likewise exercised this secondary influence. It does so in this case, and the second term in the empirical formula represents this secondary effect.

*Variation in Hydrogen Chloride.*

Having satisfactorily established the relation of the rate of change to the amount of one of the reacting substances, namely, hydrogen chlorate, we naturally sought to find the connexion between the rate and the amount of hydrogen chloride—the other reacting substance. It might be expected that the effect of variation in the hydrogen chloride would result in equations of the same form as those given above. Various series of observations were made to investigate this point. The amount of acid was varied in arithmetical progression, and the rates obtained were divided by the quantity of acid present in each case to see if anything approaching an arithmetical progression could be obtained.

No such relation appears to exist, as is shown by the following example :—

Table IV.

$$\begin{aligned} \text{HCl} &= v \times 65 \cdot 11 - 3 \times 51 \cdot 5 \text{ millionth-gram-molecules per c.c.} \\ \text{HClO}_3 &= 3 \times 51 \cdot 5 \end{aligned}$$

v.	Rate observed.	Rate	Difference (which ought to be constant).
		$v \times 65 \cdot 11 - 3 \times 51 \cdot 5$	
20	0·00739	644	86
19	0·00604	558	52
18	0·00516	506	61
17	0·00405	445	66
16	0·00331	379	69
15	0·00255	310	43
14	0·00202	267	42
13	0·00156	225	39
12	0·00117	186	30
11	0·00088	156	35
10	0·00060	121	

The first four or five numbers in the third column might perhaps be brought into an arithmetical progression without any serious alteration, but taken as a whole, the series of experimental results cannot be thus interpreted. It appears then that the effect of hydrochloric acid is not, like that of chloric acid, of two kinds, viz., (1) a primary one due to its being a decomposing substance, and (2) a secondary one of the nature above described. Yet it can hardly be supposed that it acts merely in a secondary way as a substance present and not decomposed, for its effect is proportionally much greater than that of chloric acid itself. Thus in the above series when the quantity of acid is only a little more than doubled ( $v = 10$

and  $v = 20$ ) the rate in the second case is about twelve times that in the former.

We have however proved by trial that chloric acid of itself, *without* hydrochloric acid, when mixed in the cylinder with the other ingredients, will evolve oxidising material. The rate is exceedingly slow :—

$$\begin{aligned} \text{HCl} &= 0. \\ \text{HClO}_3 &= 6 \times 51.5. & \text{Rate} &= 0.000000564. \\ \text{Temp.} &= 20^\circ. \end{aligned}$$

It is possible that two reactions are going on at the same time, one with chloric acid alone, the other substances present having merely their specific effect, and also the action between chloric acid and hydrochloric acid, both producing oxidising material.

Now amongst the various attempts made to find empirically the law of connexion between variation of hydrochloric acid and variation of rate, one result arrived at was that second differences of the rates are approximately constant. Especially is this noticeable for smaller quantities of acid. The first differences thus resemble an arithmetical progression. The next table consists of the same rates as in Table IV, compared with a series of numbers obtained by recalculation after substituting for the first differences of these a true arithmetical progression, being the one they most nearly approach. The constant difference in this case would be 0.000095. Beginning from  $v = 11$ , we get the following results :—

Table IVb.

Amount of HCl. $v$ .	Rate observed.	Rate calculated.
20	0.00739	0.00689
19	0.00604	0.00584
18	0.00516	0.00489
17	0.00405	0.00403
16	0.00331	0.00327
15	0.00255	0.00260
14	0.00202	0.00203
13	0.00156	0.00155
12	0.00117	0.00117
11	0.00088	0.00088
10	0.00060	0.00068

From  $v = 10$  to  $v = 17$ , the empirical numbers correspond fairly with the observed rates, but afterwards the latter increase more

rapidly. Now if two reactions of the nature above described are really taking place, it would lead us to conjecture a connexion expressed by the following equation :—

$$R = ku(1 + \alpha u + \beta v) + k'uv(1 + \alpha' u + \beta' v),$$

$u$  and  $v$  representing as usual the quantities of hydrogen chlorate and hydrogen chloride present, the other letters constants.

This expression is of the form

$$R = A + Bv + Cv^2,$$

when  $v$  is the only variable, and a series of such rates for which  $v$  was varied in arithmetical progression would have its second differences constant. Possibly the coefficient  $\beta$  is negative, *i.e.*, the presence of hydrogen chloride interferes with and retards the decomposition of hydrogen chlorate by itself. This would explain why, in the rates obtained with larger quantities of hydrogen chloride ( $v = 17$  to  $v = 20$ ), the ordinary formula

$$R = k'v(1 + \beta'v)$$

more nearly expresses the results obtained; the reason of this being that in the presence of a large quantity of this acid the other reaction may be altogether stopped. All this, however, is conjectural. A second series obtained could not be brought into partial agreement with the formula above; yet other mixtures of potassium chlorate and hydrogen chloride gave series of numbers of exactly the same character as this first one. These series we shall give later. The variation of the rate with the amount of hydrogen chloride present is evidently by no means a simple one. The interpretation of its complications that we have suggested can scarcely be considered fully established. It would, however, account for the facts observed.

Since in the main reaction which we desired to study, *viz.*, that between potassium chlorate and hydrogen chloride, there would be produced during the reaction some amount of potassium chloride by the decomposition of the chlorate, we determined the effect of the addition of potassium chloride to the mixture of the two acids, hydrogen chlorate and chloride.

We have already referred to the fact that in gradual reactions, such as the present, substances which remain in the solution apparently unchanged throughout the whole reaction yet exercise their specific influence, accelerating or retarding, on the velocity of the change, hence it becomes important to ascertain the effect of the potassium chloride. When the potassium chlorate and hydrogen chloride are mixed together, the latter being always in some excess, there is double decomposition, and potassium chloride and hydrogen chlorate

are formed. If the action is a complete one, all the potassium chlorate will be converted into chloric acid and potassium chloride formed in corresponding amount. There is a good deal of evidence in favour of the completeness of the decomposition in the cases we have investigated. Indeed it is perhaps to be expected *a priori* that when a stronger acid, such as our hydrochloric, is in great excess, it might entirely turn the weaker acid out of combination. If this be the case, it follows that in this reaction also the reacting substances are, as before, chloric and hydrochloric acid, and that potassium chloride is present as a "neutral" substance. At any rate, however, this compound is present to some extent in the mixture. To determine its effect mixtures of hydrogen chlorate and chloride were made, and to them quantities of potassium chloride in arithmetical progression were added, and the effect on the rate observed. The following tables show the results obtained:—

Table V.

	<i>w.</i>	R.	Difference.
HClO <sub>3</sub> = 6 × 51·5 millionth-gram-mols.	0	0·00252	0·00029
HCl = 13 × 65·11                    "	2	0·00281	0·00025
KCl = <i>w</i> × 51·5                       "	4	0·00306	0·00027
	6	0·00333	

Table VI.

	<i>w.</i>	R.	Difference.
HClO <sub>3</sub> = 3 × 51·5 millionth-gram-mols.	0	0·00335	0·0022
HCl = 16 × 65·11                    "	2	0·00357	0·0025
KCl = <i>w</i> × 51·5                       "	4	0·00382	

The effect of potassium chloride in the mixture is thus an accelerating one, and takes place in accordance with the formula already mentioned, the rates increasing in arithmetical progression approximately as the quantity of salt present is similarly increased. If  $R_w$  is the rate with a quantity  $w$  of potassium chloride,

$$R_w = A(C + \alpha w),$$

where  $A$  and  $C$  are quantities independent of  $w$ ; and  $\alpha$  is the coefficient of action; and  $A \times C = R_0$  = rate without potassium chloride.

Moreover, the addition of the potassium chloride appears to have no such disturbing effect as would result if potassium chlorate was formed to some extent as soon as the potassium chloride was added, and a condition of saline equilibrium between four substances resulted. In the first series in the above table the mixture in its last stage corresponded exactly to a mixture of potassium chlorate ( $6 \times 51.5$  millionth-gram-molecules) and hydrochloric acid ( $13 \times 65.11$ ) supposing that complete double decomposition had taken place. For comparison, therefore, a mixture was made containing initially these amounts of potassium chlorate and hydrochloric acid with this result:—

Rate obtained = 0.00337.

Rate in table = 0.00333.

This result might, of course, be taken merely to mean that the same state of saline equilibrium had been attained in both cases, but it has been already pointed out that the effect of progressive additions of potassium chloride, giving a result expressible by a formula like the above, is to show that it remains an unaltered substance in the mixture.

In the experiment detailed below, the salt was added to a mixture made with potassium chlorate and hydrochloric acid, and therefore it is presumed that it contained already some potassium chloride, obtained by saline decomposition. The results then obtained were of the same nature as before:—

Table VII.

	<i>w.</i>	<i>R.</i>	Difference.
$\text{KClO}_3 = 2 \times 51.5.$ $\text{HCl} = 16 \times 65.11 - 2 \times 51.5.$ $\text{KCl} = w \times 51.5.$	0	0.00354	0.00018
	2	0.00372	0.00022
	4	0.00394	0.00021
	6	0.00415	

It will be seen that the salt added continues to have its specific accelerative effect, and though at the end the whole quantity of potassium chloride present was  $8 \times 51.5$  millionth-gram-molecules, there is no sign whatever of the saline equilibrium being upset. The quantity of hydrochloric acid present is about double this ( $16 \times 65.11 - 2 \times 51.5$ ).

In all these experiments, the highest precision in adding the potassium chloride was not possible, as it was necessary to add the solid salt to a liquid of standard volume, and a slight variation of the conditions of the experiment besides the one contemplated was thus inevitable.



But we think there can be no doubt of the truth of the important conclusion we make from these experiments, that in all the mixtures we have made with potassium chlorate and hydrogen chloride (the molecular ratio varying from about 1 : 2 to 1 : 12) there is complete and immediate double decomposition, leaving in the mixture potassium chloride, hydrogen chlorate, and excess of hydrogen chloride; and that the reaction producing oxidising material takes place between the two acids alone.

For the facts are briefly these. Corresponding to each mixture of potassium chlorate and hydrogen chloride, we may make a mixture containing of hydrogen chlorate the amount corresponding in molecular weight to the potassium chlorate, and of hydrogen chloride the amount as before less the quantity required to decompose the potassium chlorate. Then the rate in this second mixture will be a little slower than that in the first. If now the amount of potassium chloride corresponding molecularly to the potassium chlorate be taken, divided into a small number of equal quantities, and these added separately to the second mixture, the rate will increase by an equal quantity for each addition (as upon the introduction of any neutral salt), until when all has been added the rate is approximately the same as that of the first mixture.

The following are further examples of the correspondence between the two sorts of mixtures :—

Table VIII.

I.	{	$\text{HClO}_3 = 6 \times 51.5$ millionth-gram-molecules per c.c.
		$\text{HCl} = 18 \times 65.11 - 6 \times 51.5.$
		$\text{KCl} = 6 \times 51.5.$
		Rate = 0.0105.
	{	$\text{KClO}_3 = 6 \times 51.5.$
		$\text{HCl} = 18 \times 65.11.$
		Rate = 0.0104.
II.	{	$\text{KClO}_3 = 6 \times 51.5.$
		$\text{HCl} = 15 \times 65.11.$
		Rate = 0.00554.
	{	$\text{HClO}_3 = 6 \times 51.5.$
		$\text{HCl} = 15 \times 65.11 - 6 \times 51.5.$
		$\text{KCl} = 6 \times 51.5.$
		Rate = 0.00555.
III.	{	$\text{KClO}_3 = 2 \times 51.5.$
		$\text{HCl} = 15 \times 65.11.$
		Rate = 0.00195.
	{	$\text{HClO}_3 = 2 \times 51.5.$
		$\text{HCl} = 15 \times 65.11 - 2 \times 51.5.$
		$\text{KCl} = 2 \times 51.5.$
		Rate = 0.00191.

We are now in a position to discuss the results obtained in the investigation which Mr. Harcourt originally proposed that we should make, viz., the action of hydrogen chloride on potassium chlorate.

We shall first discuss the results obtained by varying the hydrogen chloride, keeping the potassium chlorate fixed. The hydrogen chloride varied from  $v = 20$  to  $v = 10$ . After the double decomposition mentioned, the amount of acid present is  $v \times 65.11 - u \times 51.5$ . As  $u$  is constant, the acid varies in arithmetical progression. In the following table  $u = 3$ , and thus corresponds to the chloric acid results in Table IV as far as the amounts of acid go, and only differs from it in having present a certain quantity of potassium chloride. It is, therefore, to be expected that the variation will be of the same nature, and this we find to be the case.

Table IX.

$v$ .	Rate.	Rate	Difference.
		$v \times 65.11 - 3 \times 51.5$ (Dec. points omitted.)	
20	0.00876	764	93
19	0.00725	671	96
18	0.00585	575	71
17	0.00480	504	81
16	0.00374	423	52
15	0.00305	371	48
14	0.00245	323	47
13	0.00191	276	38
12	0.00149	238	42
11	0.00110	196	34
10	0.00081	162	

By inspection it will thus be seen that the third column is not an arithmetical progression. If, however, we treat the series in the other way, we find the second differences of the rate to be approximately constant. Then substituting for the first differences the nearest exact arithmetical progression and re-calculating the rates, we get a series in which the calculated and observed numbers agree fairly well between  $v = 16$  and  $v = 10$ , just as in the corresponding chloric acid series given in Table IV (*b*).

Table IXb.

Amount of hydrogen chloride. <i>v</i> .	Rate observed.	Rate calculated.
20	0·00876	0·00731
19	0·00725	0·00630
18	0·00585	0·00537
17	0·00480	0·00452
16	0·00374	0·00375
15	0·00305	0·00306
14	0·00245	0·00245
13	0·00191	0·00192
12	0·00149	0·00147
11	0·00110	0·00110
10	0·00081	0·00081

The next table contains the results obtained in a series when  $u = 4$  and  $v$  varied as before, the calculated rates are obtained in a way similar to the last, as the second differences were again approximately constant:—

Table X.

<i>v</i> .	Rate observed.	Rate calculated.
20	0·01213	0·01151
19	0·00989	0·00977
18	0·00811	0·00819
17	0·00677	0·00677
16	0·00549	0·00551
15	0·00439	0·00441
14	0·00341	0·00347
13	0·00266	0·00269
12	0·00207	0·00207
11	0·00161	0·00161
10	0·00117	0·00131

The numbers here again coincide fairly well except for the highest values of  $v$ , and this is consistent with the theory that the decomposition of chloric acid by itself is checked when the quantity of hydrochloric acid is large, for here we have a larger quantity of chloric acid produced than we had before, and a larger amount of the hydrochloric acid is required before the decomposition of the chloric acid alone is checked by the latter.

We have obtained a series in which the amount of potassium chlorate employed was as high as six units. Here, as with the case of the corresponding quantity of chloric acid, no approach to an interpretation could be attained.

All these things show that the effect of varying hydrochloric acid with chloric acid or with potassium chlorate is the same, though of what exact nature that effect is, we have not yet fully determined. No doubt the rate obtained for the decomposition of chloric acid alone is too slow to account satisfactorily for the numbers not following a law similar to that for variation in chloric acid first established.

Series of experiments were made in which the amount of potassium chlorate used was alone varied, the hydrochloric acid being constant as regards the amount added each time. It will be seen, however, from the potassium chloride results that we were not varying the potassium chlorate only in this case, but really were varying both this salt and the acid. For after saline decomposition—

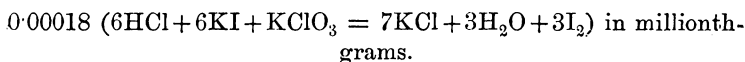
$$\begin{aligned}\text{HClO}_3 \text{ per cent.} &= u \times 51.5. \\ \text{HCl} &= v \times 65.11 - u \times 51.5.\end{aligned}$$

The variation of rates in these series, therefore, must follow a very complicated law. We have, however, drawn a series of curves, representing the variation of rate in this part of the investigation (p. 416).

The curves are thus drawn :—

A series of equidistant base lines (marked by broken lines) are taken, one base line corresponding to each quantity of hydrogen chloride used, and therefore marked at the extremity with a number representing that quantity.

Along these base lines are marked off lengths corresponding to the quantities of potassium chlorate taken, and then lengths representing the rates are measured perpendicular to these. The distance between two blue lines represents—

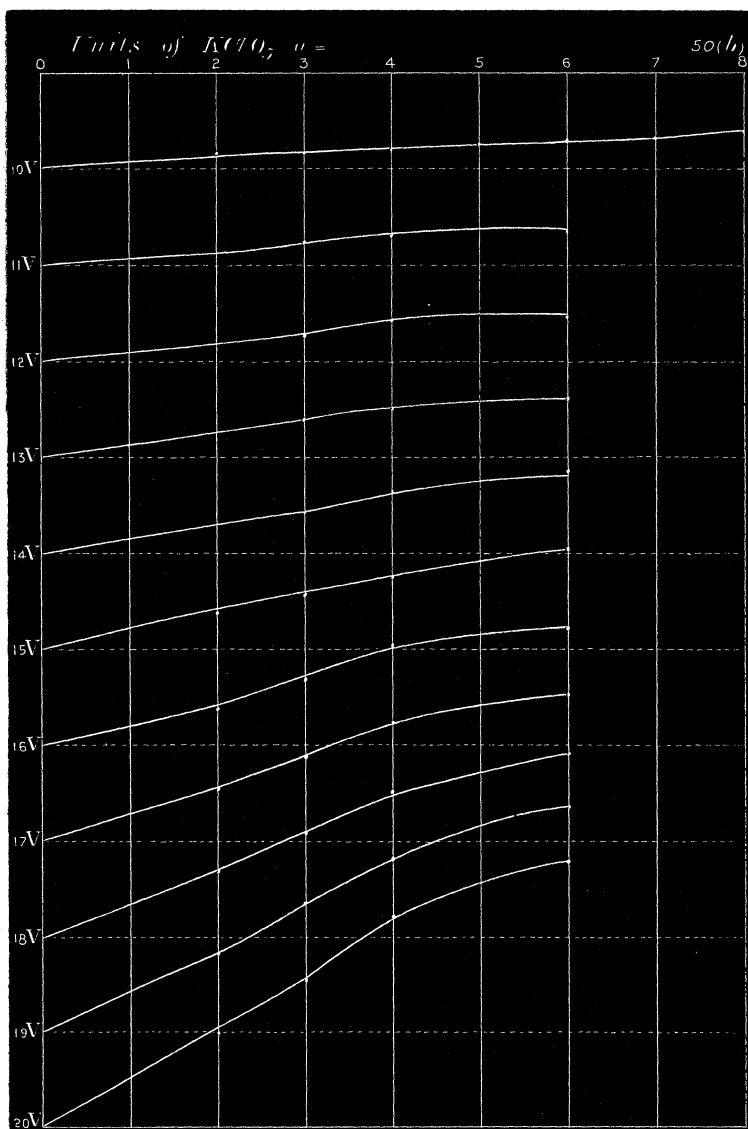


The lower curves cross the base lines above them, but this does not interfere with their comparison with the others.

It is worth observing, however, that in nearly all the cases tried,  $R/u$  decreased instead of increasing with  $u$ , after  $u = 4$  or after  $u = 5$ ; owing of course to the fact that the amount of hydrochloric acid is decreasing as  $u$  increases. In fact it may be inferred that  $dR/du$  has a root between 4 and 6.

We now turn our attention to the behaviour of another constituent of our mixture, viz., potassium iodide. We spoke of the part it played in our experiments in the introduction to our paper, but now

FIG. 2.



Curves representing the effect on the rate of variation of  $KClO_3$ . Each curve represents a certain quantity of  $HCl$  present.

we come to consider more particularly its action and the effect of its variation on the rate of decomposition.

*Variations in Potassium Iodide.*

It has been already pointed out that it is essential to the uniformity of the rate of change that there should be potassium iodide present, for in our preliminary experiments we showed that the reaction was stopped if the oxidising material was allowed to accumulate in the liquid instead of being removed by its reaction, with potassium iodide. At the same time there is no evidence to prove that potassium iodide takes part in the primary reaction. If we examine a few cases in which the amount of iodide was varied we shall soon see what sort of influence it exercises. The quantity used in all our experiments was as a rule 0.76 millionth-gram-molecule per c.c., a very small quantity in proportion to the other ingredients.

In the following table, in the initial experiment the amount used was very much smaller, 0.00946 m.g.m., and similar quantities were added one by one and their effect upon the rate ascertained.

Table XI.

	z.	R.
HCl = $15 \times 65.11$ .	1	0.00500
KClO <sub>3</sub> = $6 \times 51.5$ .	2	0.00516
KI = $z \times 0.00946$ .	3	0.00525
	4	0.00534
	5	0.00540
	6	0.00538
	7	0.00539
	8	0.00543
	9	0.00538
	10	0.00538
	11	0.00540
	12	0.00544

The rate in the same mixture in the ordinary experiments when the usual quantity (0.76 m.g.m.) of potassium iodide was introduced was 0.00554.

It thus appears that when the quantity of the substance present initially is very small, doubling the amount produces a marked increase of the rate, but after a certain amount has been added, further small quantities produce no marked result. Such a series then does not correspond to the ordinary form of variation with quantity of neutral salt, but one would be led to infer that if we call 0.0054 the normal rate we shall only get this rate when the amount of iodide present is

great enough, a retardation following any diminution of the iodide beyond this minimum necessary, and our experiments fully bear this out. The reason probably is that there is a tendency for molecules of oxidising material to begin to accumulate in the liquid if they do not immediately find molecules of potassium iodide to react with. In other words, whereas we are accustomed to consider the second reaction between chlorine or oxides of chlorine and potassium iodide, to be instantaneous, this is true only when the amount of potassium iodide present is beyond a certain minimum. In the mixture above the minimum is between 0.03784 m.g.m. and 0.0473 m.g.m. per c.c., and after that the rate of decomposition remains practically stationary until the amount present is 0.11352 m.g.m. per c.c.

The following table shows the effect of variation of iodide by larger quantities at a time, beginning with about half the usual quantity 0.76 m.g.m. per c.c.

Table XII.

	<i>z</i> .	R.
HCl = $11 \times 65.11$ .	1	0.00378
KClO <sub>3</sub> = $6 \times 51.5$ .	2	0.00389
KI = $z \times 0.367$ .	3	0.00392
	4	0.00391
	5	0.00393
	6	0.00401
	7	0.00403
	8	0.00403
	9	0.00407
	10	0.00409
	11	0.00416

There is a slight increase at the beginning of the series when the quantity of iodide is doubled; after this the rate remains practically stationary for several increments. There is, however, a marked increase between  $z = 3$  and  $z = 11$ , but not so rapid as at the beginning of the series. The reason for the indistinctness of form is evidently the fact that the effect of variation of the iodide is within the limits of experimental error. It was, therefore, deemed advisable to vary the iodide by larger quantities. In the following series single grams of the substance were introduced into the cylinder, one after the other.

Table XIII.

	<i>z.</i>	<i>R.</i>	<i>R</i> calculated as arithmetical progression.
$\text{HCl} = 15 \times 65.11.$ $\text{KClO}_3 = 6 \times 51.5.$ $\text{KI} = z \times 7.6.$	1	0.00661	0.00661
	2	0.00736	0.00725
	3	0.00786	0.00789
	4	0.00871	0.00853
	5	0.00932	0.00917
	6	0.00980	0.00981
	7	0.01043	0.01045

Here we have a series in which the rate increases distinctly with the amount of iodide, and it is not far from an arithmetical progression, certainly within the limits of experimental error. The establishment of this relation would of course show that the variation of potassium iodide has the same sort of influence as any neutral salt, and one would therefore class it with potassium chloride in this investigation. On the other hand, it seems evident that the cases are not exactly parallel; double decomposition between this salt and hydrogen chloride must go on, with a production of potassium chloride and hydrogen iodide. The hydrogen chloride present is decreased by a quantity equivalent to the amount of potassium chloride produced, and the hydrogen iodide produced will have its specific influence different from that of the former acid. At any rate one cannot be surprised at not finding the progression quite as well marked here as for potassium chloride.

We will now turn to the results obtained by varying the temperature at which we made observations. This was done in the manner described in the introduction.

#### *Variation in Temperature.*

The temperature at which most of our experiments were conducted was 20° C. We found any variation in temperature had a marked effect on the rate. A rise of temperature of 5° practically doubled the rate of decomposition, and a fall in temperature of 5° halved the rate at any point. In general if the temperature was varied in arithmetical progression the rate varied in geometrical progression. The following tables illustrate this fact:—



Table XIV.

	<i>t.</i>	R.	Ratio.
I. $\text{KClO}_3 = 6 \times 51.5$ . $\text{HCl} = 14 \times 65.11$ .	15°	0.00215	1.98
	20	0.00427	1.96
	25	0.00838	1.96
	30	0.01641	
II. $\text{KClO}_3 = 6 \times 51.5$ . $\text{HCl} = 19 \times 65.11$ .	4	0.00136	1.57
	7	0.00213	1.55
	10	0.00330	1.54
	13	0.00509	
III. $\text{KClO}_3 = 6 \times 51.5$ . $\text{HCl} = 10 \times 65.11$ .	20	0.00143	1.149
	21	0.00164	1.134
	22	0.00186	1.145
	23	0.00213	

We see from the above tables that the ratios vary with the differences between the successive temperatures. They are, however, quite independent of the quantity of each substance present. This is clearly shown in the following table, in which the rates obtained with varied quantities of potassium chlorate at 25° and 30° are compared. It will be seen that the ratio is constant. A similar result was obtained with varied quantities of potassium iodide, the ratios in this case also being independent of the amount.

Table XV.

	<i>u.</i>	Rate at 25°.	Rate at 30°.	Ratio.
$\text{HCl} = 10 \times 65.11$ . $\text{KClO}_3 = u \times 51.5$ .	3	0.00162	0.00319	1.974
	4	0.00206	0.00404	1.957
	5	0.00255	0.00502	1.966
	6	0.00301	0.00584	1.942
	7	0.00334	0.00650	1.957

It will be seen that the rate almost doubles itself for the rise of 5° between 25° and 30° in the above instances.

A great number of experiments were made in which the temperature was varied by successive differences of 3°, or 2°, or 1°; but the numbers observed could not be considered quite satisfactory owing to the intrusion of experimental errors, so it was generally found advisable to increase the temperature 5° at a time, thus making a marked difference in the rate. We deduce from this result the average value of the coefficient or ratio for the variation in temperature of 1°.

The formula embodying these results takes the same form as that in Messrs. Harcourt and Esson's reaction, in which it may be remembered the rate of decomposition doubled itself for a difference of  $10^{\circ}$  in temperature, whilst in our reaction it is doubled for every  $5^{\circ}$ .

The formula is thus expressed:—

$$R_t = R_0 e^{kt},$$

where  $t$  is temperature,  $R_0$  rate at  $0^{\circ}$ ,  $R_t$  is rate at  $t^{\circ}$ ,  $k$  is a constant. The rough approximation that the rate doubles itself for  $5^{\circ}$  would give  $k = 0.3010/5 = 0.0602$ . The value of  $k$  is determined from experiment as—

$$\frac{\log R_t - \log R_{t-5}}{5},$$

and the mean of a large number of experiments gives it as about 0.0585.

$k$  is, however, not absolutely constant, but is found to vary slightly with the temperature ( $t$ ) for which it is determined. It is larger for a low temperature range of  $5^{\circ}$ , and smaller for a difference of  $5^{\circ}$  at a higher temperature. In fact, speaking roughly, between  $0^{\circ}$  and  $15^{\circ}$  the rate is a little more than doubled by a rise of  $5^{\circ}$ ; between  $20^{\circ}$  and  $35^{\circ}$  it is a little less than doubled. The following table will show the amount of variation from this ratio:—

Table XVI.—Values of  $k$  between—

$0^{\circ}$ and $5^{\circ}$ .	$5^{\circ}$ and $10^{\circ}$ .	$10^{\circ}$ and $15^{\circ}$ .	$15^{\circ}$ and $20^{\circ}$ .
0.0643	[0.0599]	0.0610	0.0588
0.0658		0.0609	0.0605
			0.0595
$20^{\circ}$ and $25^{\circ}$ .	$25^{\circ}$ and $30^{\circ}$ .	$30^{\circ}$ and $35^{\circ}$ .	$35^{\circ}$ and $40^{\circ}$ .
0.0584	0.0584	0.0537	0.0508
0.0576	0.0592	0.0547	
0.0580	0.0583		
0.0580			
0.0586			
0.0590			
[0.0566]			

$k$  is thus seen to vary slightly with the temperatures between which it is determined. The same secondary variation was noticed by Messrs. Harcourt and Esson in their reaction. On comparing column 4 with column 5 it will be seen that their mean value is almost the same. At present it is difficult to extricate the secondary variation from experimental error, especially as a greater range of temperature

cannot be taken. At temperatures above  $35^{\circ}$  the starch-iodide colour is very difficult to perceive, as it loses its distinctive blue tinge and acquires a purple colour. At temperatures below  $0^{\circ}$ , though the starch colour is then a most beautiful blue, yet the change proceeds so slowly that it becomes difficult to hit, even within a few minutes, the point at which the blue colour has definitely appeared. Hence the range of temperature is somewhat limited.

This brings our work to a conclusion. There are several points which still need elucidation; their interpretation has seemed, so far, beyond our powers. We can only add a few facts to the pile now rapidly accumulating, out of which should grow a comprehensive theory of chemical dynamics.

The facts established by the investigation may be thus summarised:—

Dilute solutions of hydrogen chlorate and hydrogen chloride when mixed together slowly liberate oxidising material, chlorine and oxides of chlorine.

If no substance which can be oxidised is present, the accumulation of this oxidising material in the liquid soon stops the reaction.

In the presence of an iodide from which iodine can be liberated, and afterwards disposed of by means of sodium thiosulphate, the reaction proceeds regularly and with a constant velocity—constant because the quantity of the substances decomposed bears an infinitely small relation to the quantity present.

The actual rate varies with the quantity of hydrogen chlorate, in the first place *directly* as it is the substance decomposed, and in the second place with a small acceleration proportional to the quantity, the substance thus having a coefficient of acceleration independent of its being that undergoing decomposition. Thus

$$R = aQ(1 + bQ),$$

where  $R$  is rate of decomposition,  $Q$  quantity. The variation with quantity of hydrogen chloride is not of so simple a nature. This acid would seem to have (1) an effect of the secondary order above mentioned (accelerative) on the decomposition of hydrogen chlorate alone; and in addition to this (2) an effect of both primary and secondary order as above on the decomposition of hydrogen chlorate *by* hydrogen chloride.

The addition of potassium chloride to the liquid has a small accelerative effect on the rate proportional to its quantity.

If a mixture of solution of potassium chlorate and hydrogen chloride is made (in molecular proportion between 1 : 2 and 1 : 12), complete double decomposition ensues. The hydrogen chlorate formed in presence of the remaining hydrogen chloride liberates oxidising

material as above, and the potassium chloride formed exercises its specific effect on this reaction.

The small quantity of potassium iodide added for the oxidising material to work upon is not concerned in the primary reaction. The secondary action upon it producing iodine is practically instantaneous, unless its quantity is below a certain minimum. Below this there is a retardation of the velocity apparent. The effect of increasing the amount of this substance beyond the minimum is apparently analogous to that of a similar increase of any neutral salt.

The velocity of decomposition is an exponential function of the temperature; as the latter increases in arithmetical progression, the former increases in geometrical progression. The velocity is about doubled for a rise of  $5^{\circ}$  C. in temperature. The ratio in the geometrical progression is not, however, absolutely constant, but varies a little with the actual temperature. Between  $0^{\circ}$  and  $15^{\circ}$  the velocity is a little more than doubled by a rise of  $5^{\circ}$ , between  $20^{\circ}$  and  $30^{\circ}$  a little less than doubled.

FIG. 1.

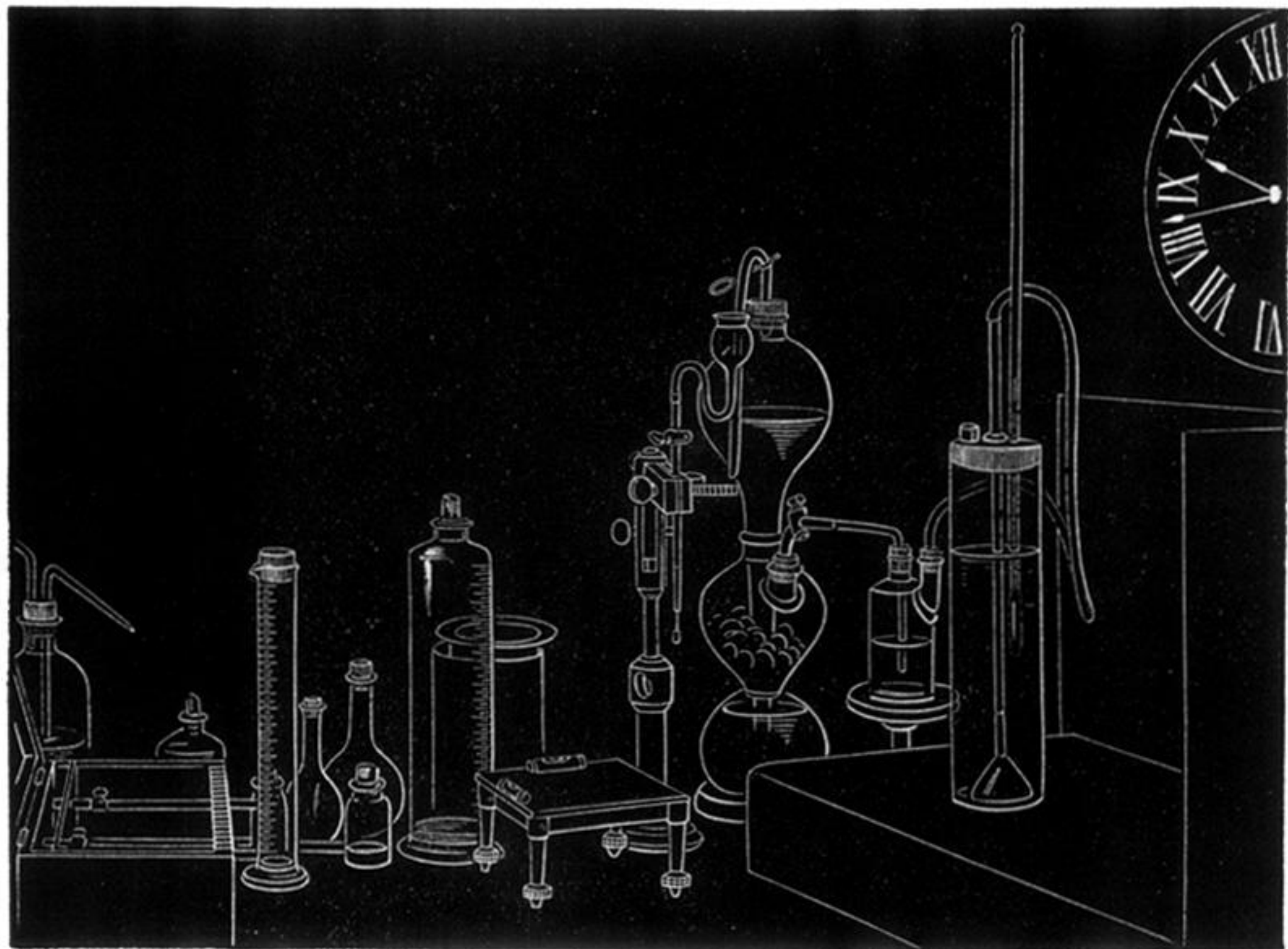
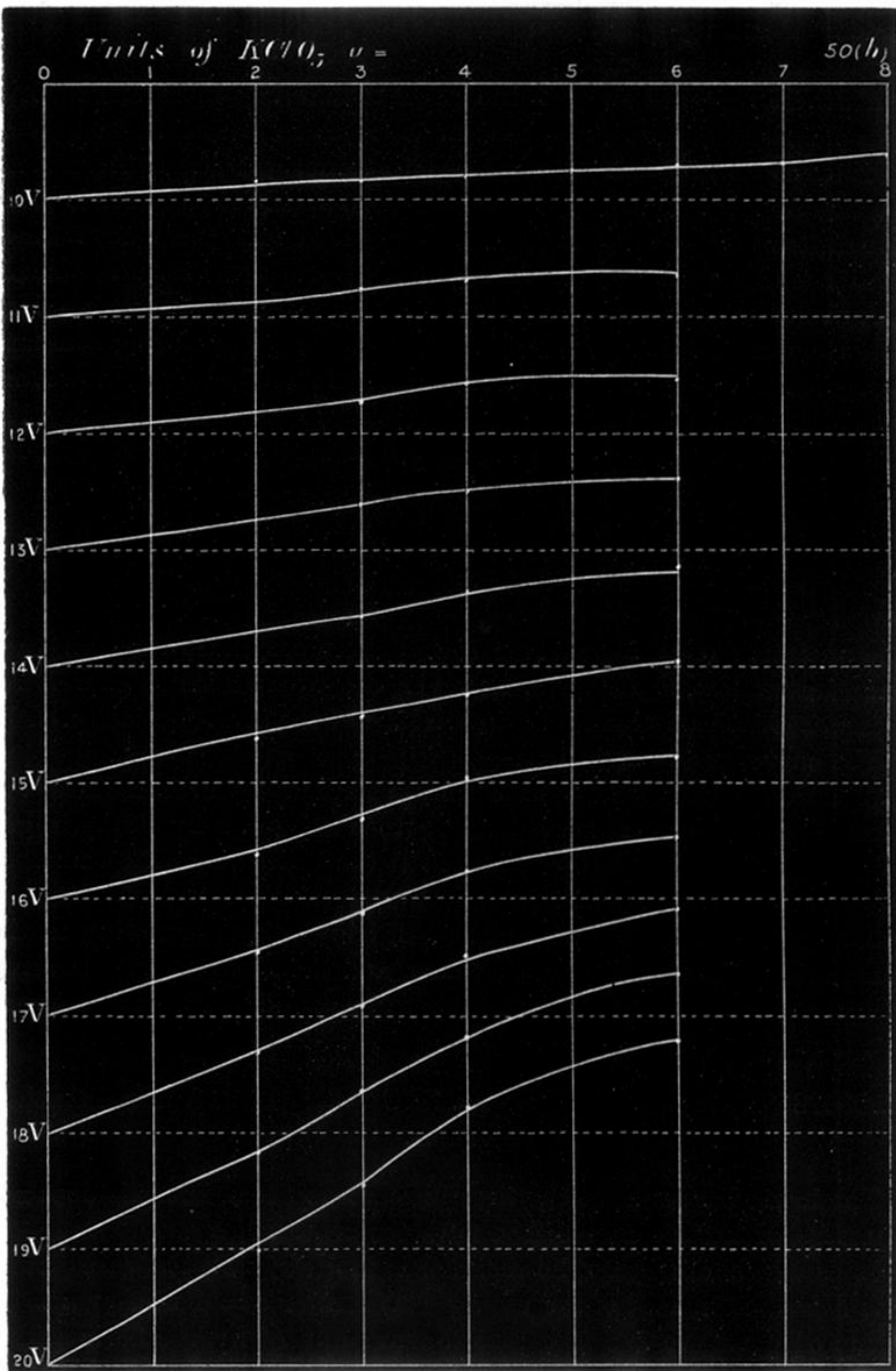


FIG. 2.



Curves representing the effect on the rate of variation of  $KClO_3$ . Each curve represents a certain quantity of HCl present.