

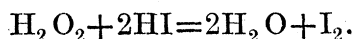
VII. *On the Laws of Connexion between the Conditions of a Chemical Change and its Amount.* By A. VERNON HARCOURT, M.A., Student of Christ Church, and Demonstrator of Chemistry in the University of Oxford, and WILLIAM ESSON, M.A., Fellow of Merton College, Oxford. Communicated by Sir B. C. BRODIE, Bart., F.R.S., Professor of Chemistry in the University of Oxford.

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II. *On the Reaction of Hydric Peroxide and Hydric Iodide.*

THE reaction of hydric permanganate upon hydric oxalate, which formed the subject of the first part of this inquiry*, having proved to be of a complex character, consisting in fact of several distinct reactions, it became necessary to seek for investigation a simpler case of chemical change. The reaction selected must at the same time combine all the other qualifications before enumerated, that it might be possible successively to vary its conditions and to measure its conditions and its amount.

After making trial of several reactions which appeared suitable, and being as often foiled by some practical difficulty in the proposed methods of investigation, we at last succeeded in devising for a very simple case of chemical change a method of investigation at once easy and exact. The reaction is that of hydric peroxide and hydric iodide,



When solutions of potassic iodide and sodic peroxide are brought together in presence either of an acid or an alkaline bicarbonate, a gradual development of iodine takes place. If sodic hyposulphite be added to the solution it reconverts the iodine, as soon as it is formed, into iodide, but appears in no other way to affect the course of the reaction. Consequently, if the peroxide be in excess over the hyposulphite, the whole of the latter is changed by the action of nascent iodine into tetrathionate, while the amount of iodide remains always constant; and after this conversion of the hyposulphite is complete, free iodine makes its appearance in the solution†. The moment at which

* Philosophical Transactions, 1866, p. 193.

† A solution of sodic hyposulphite may be mixed with a large volume of a dilute solution of potassic iodide and hydric sulphate or chloride without undergoing any decomposition. It is not oxidized to sulphate, nor acted upon in any way in this solution by hydric peroxide; for its decomposition is accompanied by a formation of sulphur, which even in very minute quantity would produce a perceptible opalescence in the liquid under observation. When hydric chloride has been employed to acidulate the solution, the addition of barium chloride after or during the set of experiments produces no precipitate. The quantity of sodic hyposulphite in the solution varies in each experiment from the maximum quantity to zero; the progress of the reaction is unaffected by this variation.

this liberation of iodine begins may be most accurately observed by the help of a little starch previously added to the liquid.

In all the experiments whose results are here recorded the same apparatus and methods were employed. The apparatus consisted of a glass cylinder about 12 inches high and 3 broad, round which, within $2\frac{1}{2}$ inches of the top, a fine line was etched: into the cylinder, through a bung closing its mouth, passed a thermometer and an inverted funnel-tube; the latter, which occupied the axis of the cylinder and reached nearly to the bottom, was connected with an apparatus for generating carbonic acid; a third hole in the bung, which served to give access to the contents of the cylinder, was ordinarily closed with a small cork. The method of performing an experiment was as follows. A quantity of water, purified from organic matter by redistillation off potassic permanganate, was boiled for some time to expel dissolved oxygen, and then allowed to cool in an atmosphere of carbonic acid. When cold it was poured into the cylinder which had previously been filled with carbonic acid, and a current of this gas, ascending in large bubbles from the inverted funnel, was kept passing through the liquid until the close of the experiment. These bubbles of gas, whose diameter is nearly half that of the cylinder, serve the purpose of stirring the fluid constantly and to any required degree, without causing loss or exposure to the air, and without danger to the thermometer. Measured quantities of the standard solutions were then introduced according to the particular experiment which was to be made; for example, 50 cub. centims. of hydric sulphate and 10 cub. centims. of potassic iodide, together with in all cases a few cub. centims. of starch. Next, the liquid having been brought to the proper temperature, the cylinder was placed on a level stand, and so much more water added as would make the upper surface of the fluid exactly coincide with the line etched upon the vessel. In every experiment the same quantity of the remaining ingredient was taken, namely, 10 cub. centims. of a dilute solution of hydric peroxide*; thus the total volume was in every experiment the same. Two operations, however, had still to be performed before starting the reaction by the addition of peroxide. First, it was necessary to make sure in each case that the fluid contained no trace of any oxidizing or reducing substance. To this end the colour of the fluid was brought to the faintest possible blue by the addition,

* The solution employed in most of these sets of experiments was prepared by dissolving a weighed quantity of pure sodic peroxide in water, and adding twice the quantity of hydric sulphate required to neutralize it. The alkaline solution of sodic peroxide, and the solution obtained by neutralizing this with hydric sulphate, decompose slowly but perceptibly from day to day; the addition of a second proportion of acid renders the solution almost absolutely stable. In some sets of experiments a pure solution of hydric peroxide was employed, which was obtained by distilling the acidified solution of sodic peroxide. The first portions of the distillate consist of water containing but little peroxide; as the acid liquid becomes more concentrated and the temperature rises, hydric peroxide comes over in considerable quantities, but finally decomposition sets in, and the liquid in the retort effervesces with escaping oxygen. About $\frac{1}{4}$ of the peroxide may thus be collected in a simple distillation. The proportion is not much increased by distilling under a diminished atmospheric pressure. It is probable that by supplying water continuously so as to keep the fluid in the retort at that degree of concentration at which the peroxide begins to come over in quantity, nearly the whole might be distilled.

according to circumstances, of a trace of sodic hyposulphite or hydric hypochlorite. If at the end of half an hour the blue tint had neither deepened nor disappeared, it was considered that the experiment might be proceeded with. Secondly, it was necessary to add a little measure of sodic hyposulphite, the first of a series of similar measures which were to play the part already indicated in the observation of the course of the reaction. These measures needed to fulfil two somewhat incompatible conditions; they must be exactly equal, or at least must stand to one another in a known ratio; and they must be of very small volume in order that their addition might not materially augment the total volume of the fluid. In the earlier experiments a pipette of about half a cubic centimetre capacity, with a capillary tube at either end, was filled with the hyposulphite solution by means of a siphon-tube provided with india-rubber nozzle and clamp. The lower end of the pipette having been wiped and pressed gently against a pad of blotting-paper, was inserted into the cylinder through the hole in the bung so as to dip beneath the surface of the fluid. By applying the mouth to a piece of india-rubber tubing slipped over the upper end of the pipette, and alternately blowing and sucking, the charge of hyposulphite was driven and completely washed into the great body of the fluid within the cylinder. This mode of measurement proved to be susceptible of great accuracy, but it only satisfied imperfectly the second condition, that of producing no material increase in the total volume of fluid used in the experiment. It will be seen that in some of the experiments hereafter recorded as many as twenty observations of the return of the blue colour were made; the total quantity of hyposulphite that had been added at the close of such an experiment was therefore 10 cub. centims., causing an increase of 1 per cent. in the volume of the fluid.

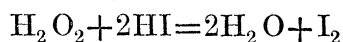
Subsequently a method of measurement was devised by which this source of error was avoided. It consisted in collecting single drops of a strong solution of hyposulphite under circumstances favourable to their perfect uniformity, and introducing these in succession into the cylinder. The drops were formed at the end of a siphon of which the shorter limb passed into a bottle containing the standard solution, while the longer limb, clamped firmly to a solid stand, was protected at its extremity by an outer tube which extended slightly below it and served to shield the growing drop from currents of air. The siphon was at one point so contracted as to deliver not more than five drops in a minute. The drops were received in small tubes about 6 inches long, open at both ends; in the side of each tube near one extremity a round hole had been blown such as would be made for the purpose of joining on another tube at right angles. Two forks were so placed on either side of the long limb of the siphon as that when one of these tubes had been passed through and rested upon them it lay horizontally just under the dropping-point, and could easily be so adjusted as to receive a drop through its lateral opening. When a drop had fallen, the tube containing it was withdrawn and replaced by another tube until a sufficient number of drops had been collected. An india-rubber cap was then slipped over the dropping-point to stop the flow of the liquid. The whole apparatus remained always in readiness, needing only the removal of its cap whenever it

was desired to collect a fresh series of drops. The width of the bottle containing the standard solution 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. Numerous determinations were made with standard iodine solution of the values of drops thus collected, and they proved to be perfectly equal. To introduce a drop into the fluid in the cylinder, the end of one of the tubes thus charged was dipped into it and moved up and down, while an active stirring was carried on by means of the bubbles of carbonic acid.

When, then, the preparations already described had been completed and a sufficient number of tubes, each loaded with its drop, were lying in readiness, it remained to add to the contents of the cylinder a measure of hydric peroxide, and to mix it as thoroughly and as rapidly as possible with the rest of the fluid. Since, however, the addition and mixing are far from being instantaneous, an experiment was not made to date from this point, but from the moment of the first appearance of the blue colour. In order that the second at which this change occurred might be accurately noted, the cylinder was placed on a sheet of white paper in a good light, and opposite to it was stationed a clock beating seconds. The paper lay on an iron plate, one end of which was heated more or less gently by a lamp according to the temperature at which the set of experiments was to be performed and that of the surrounding air. By moving the cylinder nearer to or further from the heated end of the plate, the temperature of the fluid could be conveniently regulated. The observations were made by looking down upon the column of fluid and watching the appearance of the disk forming its upper surface, listening at the same time to the beat of the clock and counting the seconds. So suddenly does the blue shade pass over the clear and brightly illuminated disk, that a practised observer can generally feel sure as to the second in which the change begins. And where the reaction is proceeding very rapidly it would often be possible to subdivide the second. As soon as the observation had been made, a drop of hyposulphite was introduced, which speedily restores the liquid to its normal colourless condition. The time that elapses between two successive appearances of the blue colour becomes continually greater as the amount of peroxide in the solution diminishes, and finally the last measure of hyposulphite requires for its conversion more iodine than the residual peroxide can furnish, and the blue colour never returns. The values of the measure of peroxide and of the drops are readily compared by means of a standard solution of potassic permanganate. To apply this reagent to the estimation of sodic hyposulphite, it is necessary to add to the solution potassic iodide and hydric sulphate, together with a little starch. The determination may thus be performed directly with the same result as though an acidified solution of potassic iodide were first decomposed by permanganate, and the liberated iodine were then used to measure the hyposulphite. The relation between the two reactions which occur simultaneously in this determination is strictly parallel to that between the reaction of hydric peroxide and hydric iodide, which forms the subject, and the reaction of iodine

and hyposulphite, which furnishes the method of our investigation. But whereas hydric peroxide acts on hydric iodide much more slowly than iodine acts on hyposulphite, hydric permanganate appears under the same circumstances to form iodine even more rapidly than it is reduced. So that in this case it is possible actually to see the double reaction, for each drop of permanganate as it enters the fluid develops for an instant the colour of iodine. But the fact of the alternate action is proved independently of this observation; for while, as has been stated, the result obtained by the addition of permanganate to the mixture of hydric iodide and hyposulphite is the same as that obtained when the two reactions are caused to occur successively, the result of the direct action of hydric permanganate on hydric hyposulphite is widely different.

The relation between the measure of peroxide and the drops of hyposulphite may also be determined in another manner. It is possible at the close of the actual set of experiments, having allowed the liquid in the cylinder to stand until the action has come practically to an end, to determine the excess of hyposulphite by means of a standard solution of iodine or permanganate, and then to determine by the same means the value of an entire drop subsequently added. Hence we know what fraction of a drop, in addition to the entire drops previously introduced, has been required to reduce the whole of the peroxide, and this quantity (the whole number and the fraction) expresses the value of the peroxide at the commencement of the experiment. If we represent by r the amount of residual hyposulphite at the close of the experiment, and by d the amount in one drop, and by n the number of drops added between the first and last appearances of the blue colour, then $\frac{r}{d}$ is the fraction of a drop which remained unacted upon, and $\frac{d-r}{d}$ is the fraction of a drop acted upon by the last portion of peroxide; and putting p equal to $\frac{d-r}{d}$, $n+p$ is the whole quantity acted on, and may therefore represent also the quantity of peroxide at the moment of the first observation. At the moment of the second observation the quantity of peroxide is $n-1+p$, and at the moments of subsequent observations it is successively $n-2+p$, $n-3+p$, &c., until finally at the moment of the last observation only p remains. Now the decrease of the peroxide is a measure of the amount of chemical change. Each time that the operation represented by



is performed a molecule of peroxide disappears. We may therefore regard the change by which $n+p$ parts of peroxide become $n-1+p$ parts as a definite portion of chemical change. Representing, then, the observed times by t_0, t_1, t_2 , &c., t_1-t_0, t_2-t_1 , &c. are the successive intervals in which as the experiment proceeds this portion of chemical change is accomplished. Now if all the conditions of the reaction could be kept constant, if it were possible to reconvert the water which is formed into hydric peroxide, as it is possible, by placing sodic hyposulphite in the solution, to reconvert the iodine which is formed into hydric iodide, then, the same event occurring always under the same con-

ditions, the intervals $t_1 - t_0$, $t_2 - t_1$, &c. would be equal. But, as it is, one condition varies, namely, the quantity of hydric peroxide in the solution; and as this quantity diminishes, the amount of chemical change in a unit of time diminishes, or the time required for the accomplishment of a unit of chemical change increases. The former of these (the amount of chemical change occurring within a given time) was the quantity which we were able to determine when investigating the reaction in which hydric permanganate is gradually reduced by an excess of hydric oxalate. The latter (the time required for a given amount of chemical change) is that which we are able to measure in the experiment which we have described. Either determination provides us with the means of calculating the relation between the amount of chemical change and the varying condition, that is, the continually diminishing amount of one of the active substances.

The following Table contains the results of one of our first sets of experiments. The standard solutions employed in it and in subsequent sets were (1) dilute hydric sulphate containing .37 grm. in a cub. centim., (2) a solution of potassic iodide containing .06 grm. in a cub. centim., (3) a solution of sodic peroxide containing .00127 grm. in the same volume. Of the first of these 100 cub. centims. were taken and 10 of each of the others. The total volume of the solution was very nearly 1 litre. The measures of hyposulphite were such that 21.45 of them were equivalent when determined by permanganate to the measure of sodic peroxide. Before starting the experiment, by adding the solution of peroxide, half a measure of hyposulphite was introduced. At the moment, then, of the first appearance of the blue colour, from which moment the observed times in column II. date, the amount of peroxide in the solution measured in drops of hyposulphite, was 20.95. The numbers in column I. express the quantities of peroxide present in the solution at the observed times, those in column IV. the intervals between two successive observations, and those in column III. the amounts of chemical change that occurred in those intervals.

We shall find it convenient to speak of such a series of observations made after the addition of successive measures of hyposulphite as a set of experiments, and to apply the term experiment to each addition of hyposulphite and the two observations which determine the corresponding interval.

TABLE I.—Weights of substances taken:—sodic peroxide .0127 grm., hydric sulphate 37.1 grms., potassic iodide .6 grm., volume of solution 993 cub. centims. Temperature 17° C.; y = residue of peroxide after t mins.; $t' - t$ = the time of a portion of chemical change by which y is diminished to y' .

| I. | II. | III. | IV. |
|-------|--------|------------|------------|
| y . | t . | $y - y'$. | $t' - t$. |
| 20.95 | 0.00 | | |
| 19.95 | 4.57 | 1 | 4.57 |
| 18.95 | 9.37 | 1 | 4.80 |
| 17.95 | 14.50 | 1 | 5.13 |
| 16.95 | 19.87 | 1 | 5.37 |
| 15.95 | 25.57 | 1 | 5.70 |
| 14.95 | 31.68 | 1 | 6.11 |
| 13.95 | 38.20 | 1 | 6.52 |
| 12.95 | 45.23 | 1 | 7.03 |
| 11.95 | 52.82 | 1 | 7.59 |
| 10.95 | 61.12 | 1 | 8.30 |
| 9.95 | 70.15 | 1 | 9.03 |
| 8.95 | 80.08 | 1 | 9.93 |
| 7.95 | 91.27 | 1 | 11.19 |
| 6.95 | 103.88 | 1 | 12.61 |
| 5.95 | 118.50 | 1 | 14.62 |
| 4.95 | 135.85 | 1 | 17.35 |
| 3.95 | 157.00 | 1 | 21.15 |
| 2.95 | 184.53 | 1 | 27.53 |
| 1.95 | 223.45 | 1 | 38.92 |
| 0.95 | 291.18 | 1 | 67.73 |

The relation between the series of numbers in these columns is represented by the curve, Plate VIII. This curve, which is drawn through twenty experimental points, corresponds to those which served in our former communication* to exhibit the rate at which hydric permanganate is reduced by hydric oxalate. Along the axis of x is measured the time of each observation, dating from the commencement of the set of experiments, and along the axis of y the amount of peroxide present in the solution at each of the times. Through each experimental point a line is drawn parallel to the axis of x to meet a line drawn through the point next below it parallel to the axis of y . These lines represent the quantities measured in each experiment, namely, the interval between two successive observations, and the amount of chemical change.

Starting, then, from the point to which our previous investigations had led us, we inquired at once whether this curve was logarithmic, that is to say, whether the amount of action had in this case varied directly with the amount of the varying active substance. The equation expressing this hypothesis has been shown† to be

$$u = ae^{-bx},$$

where a is the amount of active substance, u the residue after a time x , a the fraction disappearing in a unit of time, and e the base of Napierian logarithms. To the quantity a in this equation corresponds any of the values of y in the preceding Table, to the quantity u corresponds the next successive value of y in the Table, i. e. y' , and to the time x

* Philosophical Transactions, 1866, Plate XVIII.

† *Loc. cit.* p. 208.

corresponds the interval $t' - t$ during which the quantity y has diminished to the quantity y' . So that the modified form of the equation which is applicable to the preceding Table is

$$y' = ye^{-\alpha(t'-t)}.$$

Now this may be written in the form

$$\frac{y}{y'} = e^{\alpha(t'-t)};$$

or taking the logarithms of both sides of the equation,

$$\log \log \frac{y}{y'} = (t' - t)\alpha \log e,$$

which expresses the fact the logarithms of the ratio of any two successive residues is proportional to the corresponding interval. For calculation it is convenient to express the equation in the deduced form

$$\log \log \frac{y}{y'} - \log (t' - t) = \log \alpha + \log \log e.$$

If, then, the differences between the corresponding values of $\log \log \frac{y}{y'}$ and $\log (t' - t)$ are found to be constant within the errors of experiment, it may be presumed that the hypothesis above stated is correct.

These values and their differences are given in the following Table.

TABLE II.

| $\log \log \frac{y}{y'}.$ | $\log (t' - t).$ | $\log \log \frac{y}{y'} - \log (t' - t).$ |
|---------------------------|------------------|---|
| 2.327 | 0.660 | 3.667 |
| 2.349 | 0.681 | 3.668 |
| 2.373 | 0.710 | 3.663 |
| 2.395 | 0.730 | 3.665 |
| 2.421 | 0.756 | 3.665 |
| 2.449 | 0.786 | 3.663 |
| 2.478 | 0.814 | 3.664 |
| 2.509 | 0.847 | 3.662 |
| 2.543 | 0.880 | 3.663 |
| 2.579 | 0.919 | 3.660 |
| 2.619 | 0.956 | 3.663 |
| 2.663 | 0.997 | 3.666 |
| 2.711 | 1.049 | 3.662 |
| 2.766 | 1.101 | 3.665 |
| 2.829 | 1.165 | 3.664 |
| 2.902 | 1.239 | 3.663 |
| 2.991 | 1.325 | 3.666 |
| 1.103 | 1.440 | 3.663 |
| 1.255 | 1.590 | 3.665 |
| 1.495 | 1.831 | 3.664 |

The mean of the values of $\log \log \frac{y}{y'} - \log (t' - t)$ is $\bar{3}\cdot664$, and it will be seen that every one of the values obtained for this difference from the several experiments approximates very closely to the mean. Those which exhibit the greatest deviation on either side are $\bar{3}\cdot668$ and $\bar{3}\cdot660$; and it is important to ascertain whether these deviations can be accounted for by possible errors of experiment. The errors may occur (1) in the measurement of the small quantities of sodic hyposulphite, (2) in the management of the temperature of the solution, (3) in the estimation of the interval $t' - t$, which depends upon two successive observations of the moment at which the colour of the solution changes. If, then, we suppose that the whole deviation is due to an error committed in one of these operations, the rest having been correctly performed, we find that it might result either (1) from a particular measure of hyposulphite having been one per cent. smaller or larger than the rest, or (2) from the temperature having been $0\cdot13$ too high or too low, or (3) from an error of three seconds having been made in measuring an interval of five minutes. The second of these errors we may perhaps pronounce impossible: the fluctuations of the temperature of the solution seldom exceed $0\cdot05$, and by balancing a small oscillation on one side of the degree line by a similar oscillation on the other, the mean thermometric error during an interval may generally be reduced to a much smaller quantity. But neither of the other errors is such as might not possibly occur in one or two out of a large number of measurements and observations. It is, however, most probable that the maximum deviations from the mean result are due, not to any single experimental error, but to the simultaneous occurrence of two or more errors in the same direction. For example, it may happen (and in eleven experiments it is an even chance that the case will occur) that the measure of hyposulphite is less than the mean, the temperature of the solution too high, the first observation made too late, and the second observation too soon. All these errors conspire to make the experiment in which they occur give too high a number for $\log \log \frac{y}{y'} - \log (t' - t)$. And such a divergence as that in the experiment which gives for the value of this difference $\bar{3}\cdot668$ instead of the mean $\bar{3}\cdot664$, would occur if the measure of hyposulphite were a fifth per cent. smaller than usual, the temperature $0\cdot025$ too high, and the observed interval one second too small. Now all these errors are probable experimental errors. Hence it appears that within the limits of experimental error the numerical results here obtained accord with the hypothesis before stated. In the case of this reaction, it appears that the amount of chemical change occurring at any moment is proportional to the amount of peroxide present in the solution.

It may serve to exhibit the degree of coincidence between the experimental results and the hypothesis, if we further compare the intervals actually observed in this set of experiments with those calculated from the equation in which the hypothesis is embodied.

The general equation being $\log \log \frac{y}{y'} - \log (t' - t) = \log a + \log \log e$, and the mean

value of $\log \alpha + \log \log e$ being in this case $\bar{3}\cdot664$, the equation for calculating $t' - t$ is

$$\log (t' - t) = \log \log \frac{y}{y'} - \bar{3}\cdot664.$$

TABLE III.

| Intervals, $t' - t$. | | Intervals, $t' - t$. | |
|-----------------------|-------------|-----------------------|-------------|
| Observed. | Calculated. | Observed. | Calculated. |
| 4·57 | 4·61 | 9·03 | 9·02 |
| 4·80 | 4·84 | 9·93 | 9·98 |
| 5·13 | 5·12 | 11·19 | 11·14 |
| 5·37 | 5·38 | 12·61 | 12·65 |
| 5·70 | 5·71 | 14·62 | 14·62 |
| 6·11 | 6·09 | 17·35 | 17·30 |
| 6·52 | 6·52 | 21·15 | 21·24 |
| 7·03 | 7·00 | 27·53 | 27·48 |
| 7·59 | 7·57 | 38·92 | 39·00 |
| 8·30 | 8·23 | 67·73 | 67·73 |

In the following Table the numbers obtained in several sets of experiments are similarly compared with those calculated from equations of the same form. The sets of experiments here given are selected out of a large number equally accordant with theory, with a view to illustrate the variety of circumstances under which this reaction conforms to the law which has been enunciated. For the comparison of different sets of experiments, it will be convenient to describe each solution by stating its total volume in cubic centimetres, and how many millionths of a gramme of the several ingredients it contained in a cubic centimetre. The conditions of each set of experiments are enumerated at the head of the columns which contain the intervals actually observed and those calculated from the theoretical equation. The value of α for each set of experiments is put at the head of the column which contains the calculated intervals.

TABLE IV.

| | | | | | |
|---|--|--|---------------------------------------|--|--|
| Volume, 993 cub. centims. Temperature, 30°. Hydric sulphate, 746. Hydric iodide, 1950. Sodic peroxide, 74. Sodic hyposulphite (one measure), 13·3. | | Volume, 694 cub. centims. Temperature, 17°. Hydro-sodic carbonate, 4760. Potassic iodide, 5180. Sodic peroxide, 35·7. Sodic hyposulphite (one measure), 10·7. | | Volume, 993 cub. centims. Temperature, 0°. Hydric sulphate, 18700. Potassic iodide, 1208. Sodic peroxide, 59·5. Sodic hyposulphite (one measure), 10·9. | |
| Intervals, $t' - t$. | | Intervals, $t' - t$. | | Intervals, $t' - t$. | |
| Observed. | Calculated, $\alpha = \cdot 0242$. | Observed. | Calculated, $\alpha = \cdot 085$. | Observed. | Calculated, $\alpha = \cdot 0043$. |
| 2·42 | 2·40 | 1·17 | 1·17 | 14·27 | 13·8 |
| 2·50 | 2·55 | 1·30 | 1·30 | 14·77 | 14·6 |
| 2·71 | 2·72 | 1·45 | 1·46 | 31·38* | 32·4 |
| 2·94 | 2·91 | 1·65 | 1·66 | 17·87 | 18·1 |
| 3·10 | 3·13 | 1·93 | 1·93 | 19·62 | 19·6 |
| 3·40 | 3·39 | 2·33 | 2·32 | 21·45 | 21·4 |
| 3·68 | 3·69 | 2·88 | 2·89 | 23·65 | 23·6 |
| 4·07 | 4·05 | 3·78 | 3·83 | 26·37 | 26·3 |
| 4·52 | 4·49 | 5·70 | 5·71 | | |
| 5·02 | 5·04 | 11·73 | 11·54 | | |
| 5·77 | 5·74 | | | | |
| 6·71 | 6·67 | | | | |
| 7·92 | 7·97 | | | | |
| 9·77 | 9·88 | | | | |
| 12·91 | 13·00 | | | | |
| 19·00 | 19·00 | | | | |
| 37·00 | 36·70 | | | | |

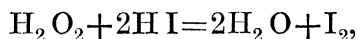
| | | | | | |
|---|--|--|--|---|---------------------------------------|
| Volume, 993 cub. centims. Temperature, 30°. Hydric sulphate, 112000. Potassic iodide, 604. Sodic peroxide, 34·9. Sodic hyposulphite (one measure), 21·9. | | Volume, 993 cub. centims. Temperature, 30°. Hydric chloride, 13900. Potassic iodide, 604. Sodic peroxide, 27·5. Sodic hyposulphite (one measure), 14·1. | | Volume, 993 cub. centims. Temperature, 50°. Hydric sulphate, 18700. Potassic iodide, 1208. Sodic peroxide, 37·8. Sodic hyposulphite (one measure), 13·4. | |
| Intervals, $t' - t$. | | Intervals, $t' - t$. | | Intervals, $t' - t$. | |
| Observed. | Calculated, $\alpha = \cdot 0949$. | Observed. | Calculated, $\alpha = \cdot 0268$. | Observed. | Calculated, $\alpha = \cdot 131$. |
| 2·31 | 2·32 | 6·53 | 6·56 | 1·00 | 1·01 |
| 2·98 | 2·98 | 8·05 | 7·96 | 1·18 | 1·17 |
| 4·15 | 4·17 | 10·13 | 10·13 | 1·37 | 1·38 |
| 7·01 | 7·00 | 13·95 | 14·00 | 1·70 | 1·70 |
| 30·38 | 30·27 | 22·42 | 22·60 | 2·20 | 2·19 |
| | | 67·08 | 66·84 | 3·08 | 3·09 |
| | | | | 5·33 | 5·32 |

The discrepancy between the observed and calculated intervals in the earlier experiments of the set made at 0° C. depends upon the difficulty which was experienced in managing the temperature. If it rose at all the rate of change was of course increased, and if it fell it was increased also by the separation of some of the water from the acid solution in the form of ice. With this exception it will be seen that the calculated and observed intervals agree very closely. Hence we conclude that whether the solution contains in each cub. centim. 746 millionths of a gramme of hydric sulphate, or 150 times that

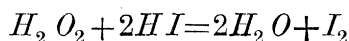
* Double interval.

quantity, 604 millionths of a gramme of potassic iodide or 9 times that quantity, or whether hydric chloride or hydro-sodic carbonate be substituted for hydric sulphate, whether the temperature be 0° or 50° C., and whether the portion of change require for its accomplishment intervals of one or two minutes, or intervals of half an hour or an hour; this reaction still conforms to the law that the amount of change is at each moment proportional to the amount of changing substance.

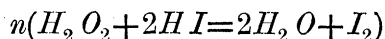
In these experiments the actual observation has been of the rate of production of iodine. But the production of this substance is only one part of the chemical change which occurs. The whole change is represented in its simplest form by the equation



and we are able, knowing the quantity of iodine that has been formed, to infer from it the quantity of water formed and the quantities of hydric peroxide and iodide that have disappeared. Now if we assign a particular weight to the molecule of iodine, the equation will represent that change by which this amount of iodine is formed, together with the proportional quantity of water, while corresponding quantities of hydric peroxide and iodide disappear. We thus obtain an expression for a particular amount of change. The unit change may be defined to be that in which 254 millionths of a gramme of iodine are formed, and when the equation written above is used to express this unit change it will be written in italics. That is to say, the expression



represents the disappearance of 34 millionths of a gramme of hydric peroxide, and of 256 millionths of a gramme of hydric iodide, and the formation of 36 millionths of a gramme of water, and 254 millionths of a gramme of iodine. The expression



represents the occurrence of n units of change. Further, since in these experiments the liquid system is homogeneous, the total change which occurs during any interval of time depends upon the quantity of change occurring in each unit of volume and the number of such units. For unit of volume we may conveniently adopt the cubic centimetre. In stating the amounts of other reagents than those which appear in the equation of the reaction, it will sometimes be convenient to express these amounts in units corresponding to those proposed above, being their molecular weights taken not as relative numbers, but as so many millionths of a gramme. For example, in enumerating the conditions of a particular experiment we shall mean by $H_2 S O_4$, or a unit of hydric sulphate, 98 millionths of a gramme of that substance; by $K I$, or a unit of potassic iodide, 266 millionths of a gramme of that salt.

In each set of experiments we commence with a system which contains elements capable of undergoing a certain quantity of change. We may express this by saying that there exists at starting a certain amount of potential change. As time elapses this potential change gradually becomes actual. From this point of view the change occurring in the system is analogous to the motion of a heavy body falling freely, which

at the commencement of its motion has a certain amount of potential energy capable of being transformed into actual energy. As the body falls the potential energy gradually becomes actual. Each experiment supplies data for the determination of the following quantities:—

- (1) The initial potential change.
- (2) The final potential change.
- (3) The actual change.
- (4) The time during which the actual change has occurred.

The relation existing between these quantities has been found to be of such a nature that the ratio of the initial and final potential changes in a given system depends only upon the time of the actual change, so that if this time is constant the ratio is constant; and since the actual change is simply the difference between the initial and final potential changes, it follows that for equal intervals of time the actual change is proportional to the initial potential change. Now if we could construct a system in which the potential change remained constant, it is clear that the actual change would proceed at a uniform rate, depending upon the quality of the system and proportional to the constant potential change. In all the systems upon which our experiments have been made the potential change varies, so that we are not able directly to observe this uniform rate, but we can obtain its value indirectly in the following way.

Suppose the time of actual change to be so small that its rate may be considered uniform during that time, the actual change will be so small that the initial and final potential changes may be considered to be equal; in other words, the potential change will be constant. The ratio of the small actual change to the time of its occurrence will thus represent the uniform rate of actual change when the potential change remains constant. The equation which connects the initial and final potential changes y, y' with the time of actual change has been found to be

$$\frac{y}{y'} = e^{\alpha(t'-t)},$$

whence we obtain

$$-\frac{dy}{dt} = \alpha y.$$

Now $-dy$ is the actual change which occurs during the time dt , and from what is stated above the ratio of these small quantities is the uniform rate of actual change when the potential change y remains constant. It follows therefore that in a given system, in which there exists a constant quantity of potential change y , the uniform rate of actual change is αy . Or since α is a constant for the given system, the rate of actual change is proportional to the potential change. If the unit of time is one minute, α represents the fraction of the potential change which is converted into actual change in one minute. We may represent what we have spoken of as potential change by writing separately the left-hand side of a chemical equation. For example, the actual change in this reaction being represented by $\text{H}_2\text{O}_2 + 2\text{HI} = 2\text{H}_2\text{O} + \text{I}_2$, the corresponding potential

change may be represented by $H_2O_2 + 2HI$, and the unit of potential change by $H_2O_2 + 2HI$. Employing this notation, the result stated above may be expressed by saying that when there exists in a system a constant quantity,

$$\begin{aligned} &y(H_2O_2 + 2HI), \\ &\alpha y(H_2O_2 + 2HI = 2H_2O + I_2) \end{aligned}$$

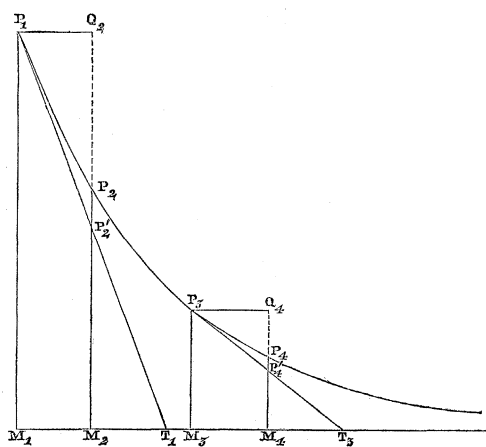
occurs in one minute. For example, in the sets of experiments recorded in Table IV., the following values were found for α , .0242, .085, .0043, .0949, .0268, .131. These numbers represent the fractions of a unit of actual change that would occur in one minute, if there existed throughout that time in each system a unit of potential change. The difference between the values of α depends, it is plain, upon the different conditions of these sets of experiments which are contrasted at the heads of the several columns.

The relation between the potential change in the system and the actual change occurring at a particular time may also be represented by supposing the rate, which up to that time has continually decreased, to become thenceforward uniform. Then the whole potential change being y , αy becomes actual in each successive minute, and the whole will have become actual, *i. e.* the reaction will have come to an end, in $\frac{1}{\alpha}$ minutes.

Whence it appears that if it were possible actually to make the rate uniform, as may approximately be done by continually raising the temperature of the solution, or otherwise compensating the diminution of peroxide, the time required for the completion of the reaction would be independent of the time at which the rate was thus modified, that is, of the amount of potential change existing in the system. For example, in the last set of experiments given in Table IV., if at any moment whatever while the reaction was proceeding the rate of change could have been made constant, in $(\frac{1}{.131} =) 7.6$ minutes from that time the whole change would have been accomplished. Whatever amount of peroxide the solution contained, this would equally have been the case; in 7.6 minutes the whole of the peroxide would have disappeared.

These results may be illustrated graphically by the following figure.

The curve $P_1P_2P_4$ represents the course of the reaction as determined by a set of experiments. M_1M_2 , M_3M_4 represent any two equal intervals of time; M_1P_1 , M_2P_2 the potential changes at the beginning and end of M_1M_2 ; M_3P_3 , M_4P_4 the potential changes at the beginning and end of M_3M_4 ; P_2Q_2 , P_4Q_4 the actual changes that have occurred during these intervals; P_1T_1 , P_3T_3 , tangents to the curve at P_1 , P_3 , represent the course of the reaction if it were to maintain the same rates with which it was proceeding at P_1 , P_3 respectively; $P_2'Q_2$, $P_4'Q_4$ the actual changes which would occur with these uniform rates during the intervals M_1M_2 ,



$M_3 M_4$, and $M_1 T_1$, $M_3 T_3$ the times in which under these circumstances the reaction would complete itself. The results arrived at are (1) $M_1 P_1 : M_2 P_2 :: M_3 P_3 : M_4 P_4$; and consequently (2) $P_2 Q_2 : M_1 P_1 :: P_4 Q_4 : M_3 P_3$, (3) $P_2' Q_2 : M_1 P_1 :: P_4' Q_4 : M_3 P_3$, (4) $M_1 T_1 = M_3 T_3$. If the interval $M_1 M_2$ be one minute and $M_1 P_1$ be the unit of potential change, then $P_2' Q_2$ represents α units of actual change.

We have thus investigated the relation existing between the amount of chemical change and the amount of hydric peroxide, and have shown that the former of these quantities varies directly with the latter. We now proceed to inquire how the amount of change is affected by the variation of the other conditions of the reaction.

For a particular system the amount of chemical change in a unit of time is expressed by αy , this expression representing the fact that if α is kept constant the amount of change varies directly with y , that is, with the amount of peroxide, and also that if y is kept constant it varies directly with α . That which has been kept constant in each set of experiments made to determine the values of y , and which is represented by α , is a group of other conditions upon which the amount of chemical change depends. The systems which have been made the subjects of experiment in this investigation have all been liquid homogeneous systems. And as the quantity of water used has been always very large in comparison with that of the various reagents, they may be further characterized as aqueous systems.

Since these systems are homogeneous, they may conveniently be described by a statement of the ingredients of their unit of volume. We adopt, as before stated, the cubic centimetre for unit of volume, and shall use the units already defined (p. 128) in the measurement of the various substances. The whole amount of chemical change is a function of all the conditions of the system in which it occurs. If we call this amount Σ , the volume of the system v , its temperature h , the time during which the change proceeds t , and the number of units $H_2 O_2$, HI , ... A , B , C , ... of the various ingredients in a unit of volume p , i , ... a , b , c , respectively, where A , B , C are units of any substance which may be introduced into the system, then

$$\Sigma = f(a, b, c, \dots h, i, \dots p, \dots t, \dots v \dots).$$

The form of this function is determinate in the case of two of these conditions, viz. t , v , and has been determined experimentally for this reaction in the case of p , so that the equation may be written in the form

$$\Sigma = p t v . f(a, b, c, \dots h, i \dots).$$

Now if we keep constant all the conditions in the undeterminate part of the function except one, say x , the form of the equation is

$$\Sigma = p t v . \phi(x),$$

the constants in $\phi(x)$ being functions of the conditions of the system which do not vary. From this equation, knowing a series of values of Σ , p , t , v , x , it is generally possible to determine the form of the unknown function. In each set of experiments made in the manner described, p and t vary while v and x remain constant, and the law of connexion

between p and t is such that the amount of change within a unit of volume in a unit of time is αp ; hence $\Sigma = \alpha p t v = p t v \cdot \phi(x)$, and therefore $\alpha = \phi(x)$. If we now make a *series* of such sets of experiments, varying x only, and determining the value of α for each set, we shall obtain a series of values of $\phi(x)$ corresponding to the several values of x , and may thence discover what function α , and therefore Σ , is of x . And if we are able thus to determine what function Σ is of each of the conditions a, b, c, \dots , we shall obtain an equation expressing the laws of connexion between all the conditions of this chemical change and its amount. It is, however, to be observed, that for the determination of α in each set of experiments it is necessary that the introduction and variation of the condition x should not alter the law of connexion between p and t . In other words, to determine $\phi(x)$ we need to obtain a series of equations of the following form,

$$\frac{p}{p'} = e^{\alpha_1(t'-t)}, \quad \frac{p}{p'} = e^{\alpha_2(t'-t)}, \quad \frac{p}{p'} = e^{\alpha_3(t'-t)} \dots$$

It is plain that the investigation of a single reaction thus considered is a work requiring the performance of a very large number of experiments. In the case before us it is possible to react with the hydric peroxide either upon hydric iodide by itself, or potassic iodide and hydric sulphate, or to substitute sodic iodide for potassic, or hydric chloride for hydric sulphate, without (as appears from the numbers in Table IV.) altering the nature of the reaction. And there is little doubt that the system might be modified by the introduction or substitution of many other substances, without affecting the chemical change, except as regards its rate. Each of the conditions thus introduced furnishes a fresh subject of inquiry, namely, as to the effect of a variation in its amount upon that of the chemical change. On the effect of varying some of these conditions of the reaction we have made numerous experiments, especially on the variation of the amounts of potassic, sodic, and hydric iodide, hydric sulphate, hydric chloride (substituted for hydric sulphate), and of the temperature of the solution. We propose to include in the present communication an account of the results we have obtained by varying in successive sets of experiments the amount of iodide.

Variation of Iodide.

When two salts are mixed in solution and no precipitation occurs, or change in the colour of the liquid, it is not possible to arrive at any probable conclusion as to the proportions or nature of the salts which the solution contains. In the greater part of the experiments about to be recorded, potassic, or sodic, or hydric iodide was added to a liquid containing an excess of hydric sulphate or chloride. Whether the systems thus formed contained the salts introduced into them, or hydric iodide and a metallic sulphate or chloride, or whether the metallic iodides were partially decomposed by the excess of free acid, we are unable to say. It may be hoped that the further investigation of the effect of varying these substances will throw light upon this question; but at present we must consider our results generally as depending upon the variation of iodide.

The following Table contains the numerical results of five sets of experiments, in each

of which the amount of actual change that would occur in a minute, the system containing constantly a unit of potential change, is determined by several experiments. The degree of coincidence of these experiments in each set may be observed by comparing the values of this amount calculated from the successive intervals on the hypothesis already established, that the actual change at any moment is proportional to the potential. The number of units of potential change at the commencement of a set of experiments is denoted by p_0 , and the number of units of actual change occurring in each experiment is denoted by a .

The volume of the solutions employed was 993 cubic centimetres, and their temperature 30° C. The actual weights of the substances taken were, in each set,

Hydric sulphate, 37.1 grms.,

Sodic peroxide, .0174 grm.,

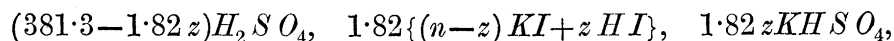
Sodic hyposulphite (one measure), .0217 grm.;

in successive sets,

Potassic iodide, .6, .9, 1.2, 1.5, 1.8 grm.

The weights of sodic peroxide and sodic hyposulphite are so small in comparison with that of the hydric sulphate, that the amount of acid neutralized by these salts is insignificant. The formation of a correspondingly small quantity of sodic sulphate may also be disregarded; for a separate experiment made with a large quantity of this salt proved that its influence upon the rate of change is very slight. But the potassic iodide was used in rather larger proportion; and it seems probable that some double decomposition occurs between it and the hydric sulphate.

Hence the permanent ingredients of a unit of volume of the system in each set of experiments were



$n(1.82KI)$ being the weight of potassic iodide taken for every cubic centimetre of the several solutions, and z being the fraction of this iodide decomposed by the hydric sulphate.

TABLE V.

| $n=2.$ $p_0=.222.$ $a=.044.$ | | $n=3.$ $p_0=.225.$ $a=.044.$ | | $n=4.$ $p_0=.222.$ $a=.044.$ | | $n=5.$ $p_0=.225.$ $a=.044.$ | | $n=6.$ $p_0=.226.$ $a=.044.$ | |
|------------------------------------|-------|------------------------------------|-------|------------------------------------|-------|------------------------------------|-------|------------------------------------|-------|
| Intervals. | $a.$ | Intervals. | $a.$ | Intervals. | $a.$ | Intervals. | $a.$ | Intervals. | $a.$ |
| 7.33 | .0302 | 4.78 | .0457 | 3.65 | .0604 | 2.87 | .0757 | 2.35 | .0923 |
| 9.4 | .0302 | 6.14 | .0455 | 4.73 | .0600 | 3.68 | .0755 | 3.10 | .0895 |
| 35.47 | .0301 | 8.61 | .0452 | 6.59 | .0604 | 5.12 | .0757 | 4.25 | .0906 |
| 103.63 | .0303 | 14.39 | .0449 | 11.16 | .0601 | 8.55 | .0748 | 7.05 | .0900 |
| | | 53.26 | .0451 | 52.20 | .0601 | 29.78 | .0762 | 23.97 | .0902 |

The values obtained for a from the different experiments of each set are fairly concordant, and we may therefore assume their mean to be the true value. It is at once evident that these numbers are in arithmetical progression, and bear to one another the same ratios as the values of n , viz., 2 : 3 : 4 : 5 : 6. They are compared below with a series of numbers calculated on this hypothesis.

TABLE VI.

| <i>n.</i> | <i>a.</i> Observed. | <i>a.</i> Calculated. |
|-----------|------------------------|--------------------------|
| 1 | | ·0151 |
| 2 | ·0302 | ·0302 |
| 3 | ·0453 | ·0453 |
| 4 | ·0602 | ·0604 |
| 5 | ·0756 | ·0755 |
| 6 | ·0905 | ·0906 |

To confirm this result a second series of sets of experiments was made, differing from the former by the substitution of hydric chloride for hydric sulphate. Comparing equivalent quantities, it had been observed that hydric chloride increases the rate of change nearly twice as much as hydric sulphate. Therefore, in order to obtain a sufficient series of different rates of which the first should not be inconveniently small, nor the last inconveniently great, one molecule or half an equivalent of hydric chloride was substituted for a molecule of hydric sulphate.

Volume of the solutions 993 cub. centims., temperature 30° C.

Actual weights of substances taken in each set:

Hydric chloride, 13·8 grms.,

Sodic peroxide, ·0257 gm.,

Sodic hyposulphite (one measure), ·0135 gm. ;

in successive sets,

Potassic iodide, ·3, ·6, ·9, 1·2, 1·5, 1·8, 2·1, 2·4 grms.

Hence the permanent ingredients of a unit of volume of the system in each set of experiments were

$$(381·3 - 1·82z)HCl, \quad 1·82((n-z)KI + zHI), \quad 1·82zKCl.$$

TABLE VII.

| <i>n</i> = 1. <i>p</i> ₀ = ·16. <i>a</i> = ·0274. | | <i>n</i> = 2. <i>p</i> ₀ = ·17. <i>a</i> = ·0274. | | <i>n</i> = 3. <i>p</i> ₀ = ·166. <i>a</i> = ·0274. | | <i>n</i> = 4. <i>p</i> ₀ = ·165. <i>a</i> = ·0274. | |
|---|-----------|---|-----------|---|-----------|---|-----------|
| Intervals. | <i>a.</i> | Intervals. | <i>a.</i> | Intervals. | <i>a.</i> | Intervals. | <i>a.</i> |
| 13·82 | ·0136 | 6·53 | ·0269 | 4·43 | ·0406 | 3·38 | ·0537 |
| 16·83 | ·0137 | 8·05 | ·0265 | 5·47 | ·0402 | 4·20 | ·0528 |
| 21·42 | ·0140 | 10·13 | ·0268 | 6·93 | ·0406 | 5·38 | ·0531 |
| 32·83 | ·0132 | 13·95 | ·0269 | 9·82 | ·0401 | 7·25 | ·0555 |
| | | 22·42 | ·0270 | 16·27 | ·0406 | 12·65 | ·0540 |
| | | 67·08 | ·0267 | | | | |
| <i>n</i> = 5. <i>p</i> ₀ = ·164. <i>a</i> = ·0274. | | <i>n</i> = 6. <i>p</i> ₀ = ·164. <i>a</i> = ·0274. | | <i>n</i> = 7. <i>p</i> ₀ = ·163. <i>a</i> = ·0274. | | <i>n</i> = 8. <i>p</i> ₀ = ·161. <i>a</i> = ·0274. | |
| Intervals. | <i>a.</i> | Intervals. | <i>a.</i> | Intervals. | <i>a.</i> | Intervals. | <i>a.</i> |
| 2·68 | ·0681 | 2·28 | ·0802 | 1·92 | ·0957 | 1 68 | ·111 |
| 3·35 | ·0666 | 2·77 | ·0809 | 2·40 | ·0940 | 2·17 | ·106 |
| | | 3·62 | ·0798 | 3·07 | ·0951 | 2·75 | ·108 |
| 6·05 | ·0670 | 5·05 | ·0809 | 4·40 | ·0942 | 4·02 | ·106 |
| 10·32 | ·0671 | 8·78 | ·0802 | 7·58 | ·0948 | 7·00 | ·108 |

The mean values of α derived from these sets of experiments are compared in the following Table with a series calculated from the equation $\alpha = \cdot 01347n$.

TABLE VIII.

| <i>n.</i> | α Observed. | α Calculated. |
|-----------|-----------------------|-------------------------|
| 1 | $\cdot 0136$ | $\cdot 0135$ |
| 2 | $\cdot 0268$ | $\cdot 0269$ |
| 3 | $\cdot 0404$ | $\cdot 0404$ |
| 4 | $\cdot 0538$ | $\cdot 0539$ |
| 5 | $\cdot 0672$ | $\cdot 0673$ |
| 6 | $\cdot 0804$ | $\cdot 0808$ |
| 7 | $\cdot 0948$ | $\cdot 0943$ |
| 8 | $\cdot 1080$ | $\cdot 1078$ |

Thus it appears that the amount of chemical change occurring in the solutions at any moment varies directly with the amount of iodide, if all the other conditions are the same. A few of the numbers from which the mean values of α are obtained differ considerably one from another. These differences were generally due to observed errors in the management of the temperature of the solution, which having through inadvertence risen or fallen a little during one interval, was made to fall or rise in a corresponding degree during the next interval, that the mean result might be correct.

In both these series the quantity of iodide was small in proportion to the quantity of acid, amounting at the most to 4 per cent. Two sets of experiments were subsequently made with systems containing in a cubic centimetre $54\cdot 5$ H_2SO_4 , and $10\cdot 42$, $20\cdot 84$ KI respectively, at a temperature of 17° C. The values of α given by these two sets were $\cdot 0116$ and $\cdot 0243$, the latter of which is considerably more than double the former. In some other sets of experiments, in which instead of a metallic iodide different quantities of hydric iodide were added to the solutions, it was observed similarly that the increase in the rate of change was more than proportional to the increase of hydric iodide. Now, since it appears that hydric sulphate or hydric chloride, though playing no immediate part in the reaction, yet accelerates its course, it seems reasonable to suppose that a double effect may be produced by the addition of hydric iodide. For while on the one hand this addition increases the amount of substance which the hydric peroxide has to act upon, on the other hand, like the addition of hydric sulphate or hydric chloride, it increases the acidity of the solution. But further, the rate of change depends not only upon the acidity of the solution, but upon the particular acid which it contains. The two acids upon which we have experimented affect the rate of change in different degrees, hydric chloride exercising a greater influence than hydric sulphate; so that if we were to add a quantity of neutral chloride to a solution containing hydric sulphate, we should doubtless increase the rate of change; for some of the hydric sulphate would be replaced by its equivalent (in the ordinary chemical sense) of hydric chloride. In the same way it is probable that a solution into which hydric sulphate and potassic iodide have been introduced contains some hydric iodide, and that this acid also has its particular effect

upon the rate of change independently of the part which it plays in the reaction itself. Now, if equivalent quantities of hydric sulphate and iodide caused equal accelerations, the replacement in the solution of one of these acids by the other would produce no effect; but if hydric iodide, like hydric chloride, has a greater accelerating power than hydric sulphate, the effect of this replacement would be to cause an acceleration independent of and additional to that which is due to the increase of iodide. When, as in the sets of experiments recorded in Tables V. and VII., the hydric sulphate or chloride replaced by hydric iodide is but a small fraction of the whole amount in the solution, this change does not so affect the rates as to hinder us from observing the result of the simple variation of iodide; but when the experiment is pushed further, and a considerable proportion of the acid is thus changed, the effect of this second variation becomes perceptible. With the view of inquiring whether the proportional relation between the amount of iodide and the amount of chemical change still holds good when the solution does not contain an excess of acid, a number of sets of experiments were made with a constant quantity of hydric iodide and various quantities of potassic iodide. Here we encountered a fresh difficulty; the primary reaction no longer followed the law expressed by the equation $\frac{y}{y'} = e^{\alpha(t'-t)}$; and although the measurements of the solutions

and the observation of the intervals were made with all possible care, we are not able to derive from the experimental data any series of values for α , nor therefore to determine what function the total amount of change was of the amount of iodide. The following Table contains the results of these sets of experiments. To avoid the introduction of any other acid besides hydric iodide, a neutral solution of hydric peroxide was used.

The volume of the solutions was 993 cub. centims., and their temperature 30° C.

The amount of iodide in a cubic centimetre of each was 15.25 *HI* and 7.28 *n KI*. The amount of peroxide at starting was about .98 $H_2 O_2$. The amount of actual change during each interval was .13{ $H_2 O_2 + 2HI = 2H_2 O + I_2$ }.

TABLE IX.

| <i>n</i> =0. | <i>n</i> =1. | <i>n</i> =2. | <i>n</i> =3. | <i>n</i> =4. | <i>n</i> =5. | <i>n</i> =6. |
|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Observed intervals. | Observed intervals. | Observed intervals. | Observed intervals. | Observed intervals. | Observed intervals. | Observed intervals. |
| 6.40 | 4.05 | 2.93 | 2.28 | 1.85 | 1.55 | 1.38 |
| 7.40 | 4.90 | 3.54 | 2.75 | 2.25 | 1.92 | 1.72 |
| 9.05 | 5.92 | 4.33 | 3.50 | 2.82 | 2.40 | 2.13 |
| 11.27 | 7.58 | 5.70 | 4.65 | 3.76 | 3.26 | 2.95 |
| 15.30 | 10.57 | 8.15 | 6.80 | 5.52 | 4.74 | 4.32 |
| 24.30 | 17.41 | 13.82 | 12.20 | 9.65 | 8.06 | 7.93 |
| 59.82 | 56.07 | | | | | |

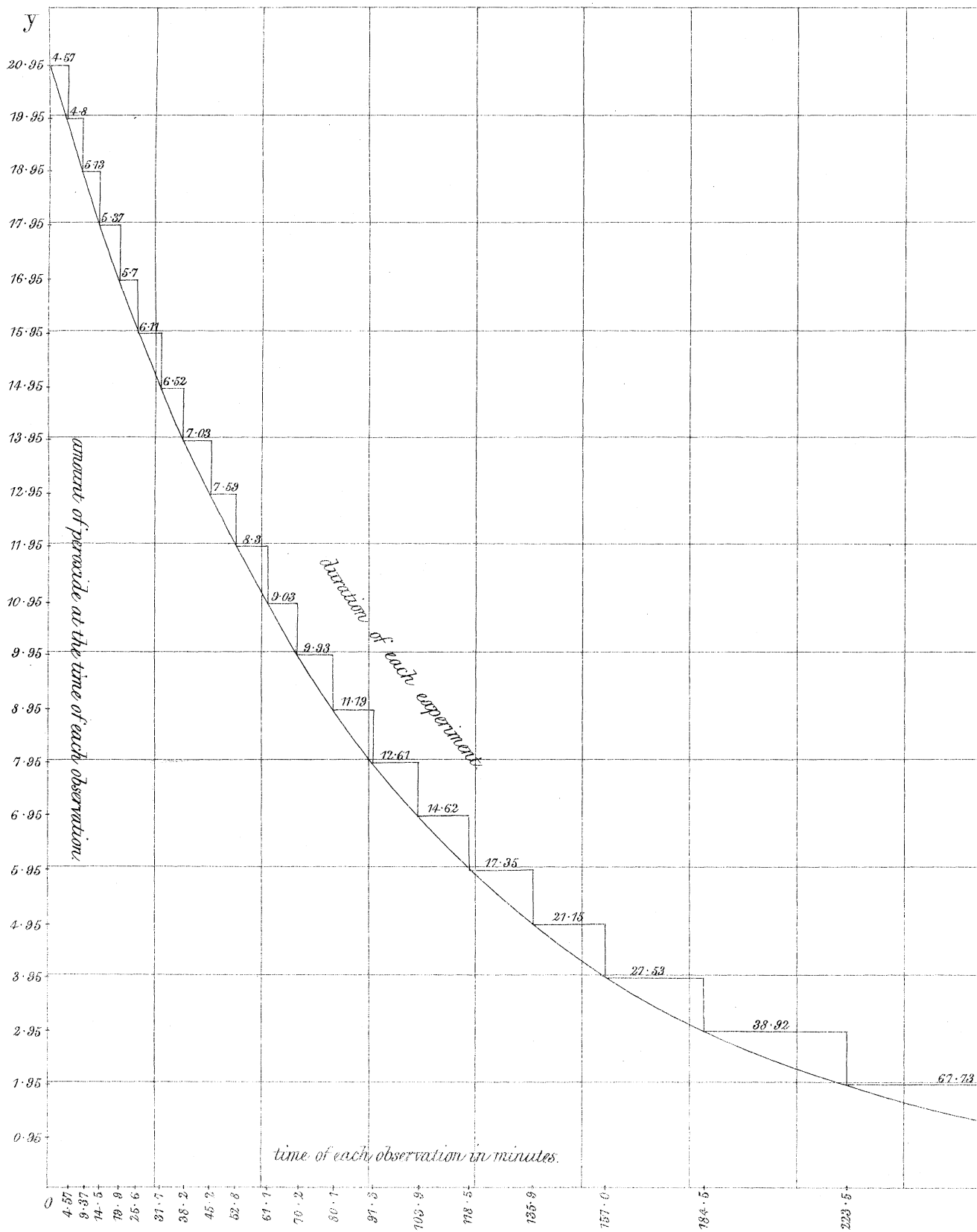
The first, and perhaps the second of these sets of experiments, gives a logarithmic curve; the remainder depart more and more widely from this relation. The cause of the departure is probably the same as that which prevented the observation of the law of

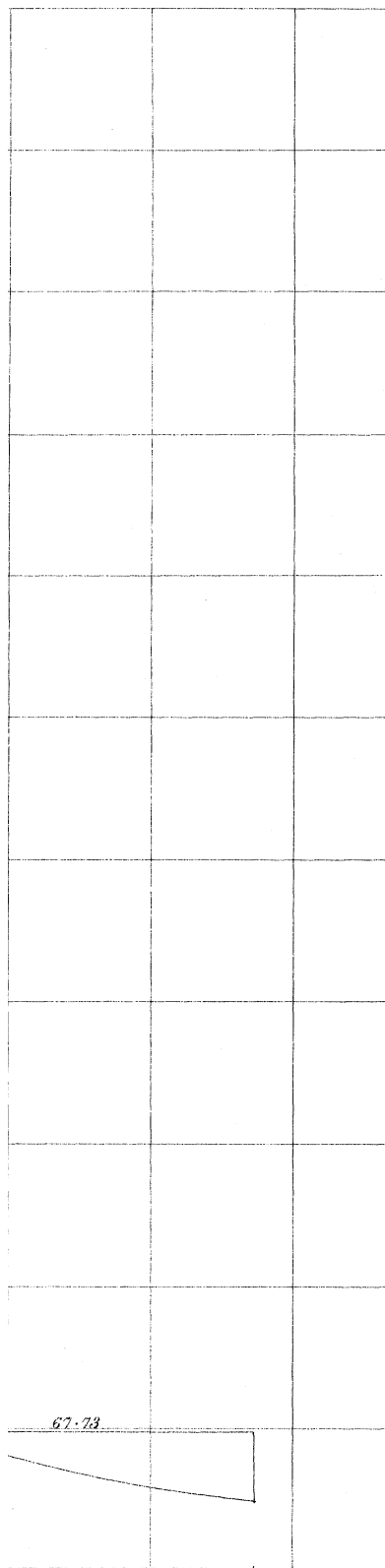
proportionality in the case of the reaction of hydric oxalate and permanganate. The measurements are no longer of the course of a single gradual action. The several series might be represented by equations expressing such a complication as it is most likely occurs, *e. g.*, the gradual oxidation of potassic iodide to iodate, and the gradual reduction of this salt by hydric iodide. But the constants of such equations cannot be determined from the experimental numbers with sufficient accuracy for much reliance to be placed upon them.

In consequence therefore of these two facts,—that the amount of change is a function both of the kind and of the amount of acid in the solution, and that the nature of the reaction is changed when a mixture of hydric and potassic iodide is used,—we have only been able to investigate the relation which exists between the amount of iodide in the solution and the amount of change in a particular case, namely, when the solution contains a sufficient quantity of free acid to render immaterial the replacement of a little of it by hydric iodide, and to determine sharply the occurrence of the single reaction, $\text{H}_2\text{O}_2 + 2\text{HI} = 2\text{H}_2\text{O} + \text{I}_2$. With this limitation, the form of the function $\phi(i)$ in the expression $\Sigma = ptv \cdot \phi(i)$ has been established by the foregoing experiments, and we may now write the general equation in the form

$$\Sigma = iptv \cdot f(a, b, c, \dots).$$

That is to say, the amount of change varies directly, (1) with the amount of iodide, and (2) with the amount of peroxide in a unit volume of the solution; (3) with the time during which the change proceeds; (4) with the total volume of the solution; and, finally, with some function of each of the other conditions under which the change occurs.





284.2

x

