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# Bakerian Lecture: On the Laws of Connexion between the Conditions of a Chemical Change and Its Amount. III. Further Researches on the Reaction of Hydrogen Dioxide and Hydrogen Iodide

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*Phil. Trans. R. Soc. Lond. A* 1895 **186**, 817-895
doi: 10.1098/rsta.1895.0022

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# XXII. Bakerian Lecture.—*On the Laws of Connexion between the Conditions of a Chemical Change and its Amount.*—III. *Further Researches on the Reaction of Hydrogen Dioxide and Hydrogen Iodide.*

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Received March 15,—Read May 9, 1895.

Nearly thirty years ago we laid before the Royal Society the results of our inquiries into two cases of gradual chemical change, viz.: (1) the reaction of hydrogen permanganate and hydrogen oxalate, and (2) the reaction of hydrogen dioxide and hydrogen iodide.*

We have continued at intervals our investigation into the latter reaction, and have obtained some further results, which we desire now to communicate to the Royal Society.

The manner in which our observations were made is fully described in the previous paper, to which we hope the reader will refer; but it may be convenient after so long an interval again to describe briefly our mode of observing and of calculating the rate of change. The vessel employed consisted of a tall glass cylinder, 12 × 3 inches, round which, about $2\frac{1}{2}$ inches from the top, a fine line had been etched. The cylinder was closed by a caoutchouc stopper, through which passed (1) an inverted funnel-tube in the centre, (2) a thermometer, (3) a short tube, $1 \times \frac{1}{2}$ inch, giving access to the interior. Into the cylinder were poured water and measured quantities of solutions of all the reacting substances except hydrogen dioxide; the temperature was brought to the desired degree; and more water was added till the upper surface of the liquid coincided with the line round the cylinder. Then a measure of hydrogen dioxide was brought in. Large bubbles of carbonic acid were sent from the funnel-tube through the liquid to act as a stirrer. To provide for the ready addition from time to time of equal quantities of sodium thiosulphate, by which the change is measured, without materially altering by these additions the total volume of liquid, single drops of a strong solution of the salt were collected in tubes about 6 inches long, which could be dipped into the cylinder through the short tube. These drops, which were found to be exceedingly uniform, were brought one at a time into the liquid whenever it showed the blue colour of iodized starch. Each drop removed the

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* 'Philosophical Transactions,' vol. 156, p. 193, and vol. 157, p. 117. Also 'Journal of the Chemical Society,' vol. 20, p. 460.

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iodine which had been formed since the change of colour was previously observed, and, subsequently, so much of the iodine which was continually being formed as it was capable of reacting with. As soon as the small portion of thiosulphate was exhausted, iodine was no longer removed, the liquid became blue again, and the moment of change was noted. Thus were observed the successive intervals required for the performance of a known fraction of the total change, and from these the rate of the change was inferred. 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 thiosulphate requires for conversion into tetrathionate more iodine than the residual peroxide can furnish, and the blue colour does not return. After many hours the excess of thiosulphate was determined by means of a dilute solution of iodine; one or more drops of thiosulphate were then brought into the liquid and determined in the same manner. These observations give the value of one drop and of the remainder of the last drop in terms of the solution of iodine; calling the first of these $d$, the second $r$, and the number of drops added between the first and last appearances of the blue colour $n$, $r/d$ is the fraction of a drop which remained unacted upon, and $(d-r)/d$ is the fraction of a drop acted upon by the last portion of peroxide. Thus the amount of peroxide originally taken is $n+(d-r)/d$, and of this in each observed interval an unit disappeared, the unit being the mass of peroxide which reacts with the mass of thiosulphate dissolved in one drop.

These observations furnish the means of measuring the time required for a definite amount of chemical change under known conditions. The time required varied because one condition was continually varying, namely, the amount of peroxide in the liquid.

If $y$ is the amount of peroxide at a time $t$, $y'$ at a time $t'$, the relation connecting these quantities is

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

in which $\alpha$ is the fraction of the peroxide which disappears in an unit of time. Each observation furnishes a value of $\alpha$, and the mean of the values so obtained from a set of observations is taken as the true value under the conditions of each experiment.

In our former paper the effect of varying two of the conditions of the reaction is established, namely, that the amount of change is directly proportional (1) to the amount of dioxide, and (2) to the amount of iodide in one volume of the solution. Since the amount of change is also directly proportional to the number of volumes, or total volume, of the solution, and to the time during which the change proceeds, we expressed the whole amount of change under any conditions of the reaction by the equation

$$\Sigma = ditv \,.\, f(a, b, c, \ldots),$$

where $d$ represents the amount of dioxide, $i$ the amount of iodide in an unit volume

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of the solution, $t$ the time during which the change proceeds, $v$ the number of unit volumes or total volume of the solution, and $a, b, c, \ldots$ other conditions of the change.

Of these other conditions two only are necessary conditions of the change, temperature, and the presence of water; but the addition to the solution of other substances which play no part in the final reaction affects the rate at which the change proceeds, and thus a very large number of observations may be made of the influence which different substances exercise upon the rate of one chemical change, furnishing a basis for the comparison and classification of such substances.

In all the experiments here recorded one of the reacting substances has been either hydrogen dioxide, or sodium dioxide, and the other either hydrogen iodide, sodium iodide, or potassium iodide. Beside these, water has always been present, and, as a rule, in preponderating quantity. Other substances added in different series of experiments have been hydrogen sulphate, hydrogen chloride, sodium hydrogen carbonate, sodium chloride, sodium sulphate. None of these substances, as far as we know, any more than the water which they replace, participates directly in the reaction. We have also made sets of observations at different temperatures with the view of determining the relation between this condition of the reaction and the rate of change.

As in our former paper, we express the conditions of each experiment by stating the temperature and the amount of each ingredient in 1 cub. centim. of the solution; and in order to present at once known masses and atomic or molecular proportions, we use the symbol $H$ to express one-millionth of a gram of hydrogen, and the other chemical symbols italicized to express the corresponding atomic masses; for example $H^2SO^4$ stands for 98 millionths of a gram, or ·098 milligram of hydrogen sulphate. The actual volume of solution used (which was rather less than 1 litre) and the actual weights of the substances dissolved, are only material as furnishing the data for calculating the ingredients of an unit volume. The rate of change, being the ratio of actual to potential change, is the same in a litre and in a cubic centimetre.

It has been shown in the previous paper that if $y_0\,(H^2O^2 + 2HI = I^2 + 2H^2O)$ is the amount of potential change at a time $t_0$, and $y_1\,(H^2O^2 + 2HI = I^2 + 2H^2O)$ is the amount of potential change at a time $t_1$, the quantities $y_0$, $y_1$, $t_0$, $t_1$, are connected by the equation given above,

$$y_1 = y_0\, e^{-\alpha(t_1 - t_0)},$$

$y_0 - y_1$ being the number of units of actual change which have taken place during the interval $t_1 - t_0$. If the interval $t_1 - t_0$ is diminished without limit, the ratio $\frac{y_0 - y_1}{t_1 - t_0}$ is equal to $\alpha y_0$. That is to say, the amount of change occurring at every moment is in a constant ratio to the remaining amount of potential change.

The substances used in most of our sets of observations were (1) a solution containing hydrogen dioxide, made by dissolving sodium dioxide in a slight excess

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of dilute hydrogen sulphate; (2) a solution of potassium iodide or hydrogen iodide; and (3) dilute hydrogen sulphate. Of the last-named acid a relatively large quantity was generally taken, varying from 1 cub. centim. to 60 cub. centims. of concentrated sulphuric acid.

### *Variation of Hydrogen Sulphate.*

The following observations were made in order to ascertain the influence on the rate of change of variations in the amount of hydrogen sulphate. At the head of Table I. the absolute quantities of each substance are stated as numbers of millionth-gram molecules per cub. centim., $n$ being the quantity varied in successive experiments, and $z$ the unknown fraction of the potassium iodide taken, which, in each experiment, undergoes the decomposition

$$\mathrm{KI} + \mathrm{H^2SO^4} = \mathrm{HI} + \mathrm{KH\,SO^4}.$$

The temperature of the solutions was in every case 30° C. The numbers represented as $y_0$ are the numbers of drops of thiosulphate required to reduce all the iodine formed in the course of each experiment by the measure of hydrogen dioxide taken. The intervals between successive observations are expressed in minutes; and $\alpha$ is the fraction of the hydrogen peroxide present at any moment, which would be decomposed if the amount present at that moment were kept constant for one minute.

TABLE I.

$(38{\cdot}1n - 3{\cdot}64z)\,H^2SO^4,\quad 3{\cdot}64\,\{(1-z)\,KI + zHI\},\quad 3{\cdot}64zKHSO^4,$
$(55400 - 65n)\,H^2O.$ Temperature 30° C.

| $n = 5$, $y_0 = 11{\cdot}2$. | | $n = 6$, $y_0 = 11{\cdot}64$. | | $n = 7$, $y_0 = 11{\cdot}7$. | | $n = 8$, $y_0 = 11{\cdot}7$. | | $n = 9$, $y_0 = 11{\cdot}67$. | |
|---|---|---|---|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 5′·32 | ·0175 | 4′·47 | ·0201 | 3′·98 | ·0224 | 3′·62 | ·0245 | 3′·32 | ·0270 |
| 5·88 | ·0175 | 4·96 | ·0199 | 4·44 | ·0221 | 3·96 | ·0247 | 3·63 | ·0271 |
| 6·52 | ·0177 | 5·50 | ·0199 | 4·90 | ·0222 | 4·44 | ·0245 | 4·05 | ·0270 |
| 7·45 | ·0175 | 6·19 | ·0199 | 5·53 | ·0220 | 4·96 | ·0246 | 4·53 | ·0270 |
| 8·51 | ·0175 | 7·06 | ·0199 | 6·30 | ·0221 | 5·67 | ·0245 | 5·20 | ·0269 |
| 10·05 | ·0175 | 8·19 | ·0200 | 7·28 | ·0222 | 6·58 | ·0245 | 6·02 | ·0269 |
| 12·17 | ·0175 | 9·75 | ·0200 | | | 7·90 | ·0244 | 7·22 | ·0269 |
| 15·47 | ·0175 | 12·08 | ·0201 | | | 9·70 | ·0247 | 8·91 | ·0270 |
| 21·30 | ·0176 | 15·88 | ·0202 | | | 12·87 | ·0244 | 11·82 | ·0269 |
| | | 23·80 | ·0200 | | | 18·85 | ·0245 | 17·38 | ·0270 |
| | | 47·45 | ·0199 | | | 36·15 | ·0245 | 33·95 | ·0269 |
| Mean rate ·0175 | | Mean rate ·0200 | | Mean rate ·0222 | | Mean rate ·0245 | | Mean rate ·0270 | |

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TABLE I.—(continued).

| $n = 10$,<br>$y_0 = 11·19$. | | $n = 11$,<br>$y_0 = 11·7$. | | $n = 12$,<br>$y_0 = 11·16$. | | $n = 15$,<br>$y_0 = 11·15$. | | $n = 16$,<br>$y_0 = 11·17$. | |
|---|---|---|---|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 3′·42 | ·0302 | 2′·78 | ·0321 | 2′·65 | ·0354 | 2′·18 | ·0429 | 2′·02 | ·0464 |
| 3·83 | ·0301 | 3·02 | ·0324 | 2·93 | ·0353 | 2·44 | ·0426 | 2·21 | ·0469 |
| 4·33 | ·0301 | 3·35 | ·0324 | 3·32 | ·0348 | 2·70 | ·0428 | 2·49 | ·0463 |
| 4·95 | ·0302 | 3·75 | ·0325 | 3·75 | ·0348 | 3·03 | ·0432 | 2·78 | ·0470 |
| 5·82 | ·0303 | 4·28 | ·0325 | 4·30 | ·0350 | 3·50 | ·0430 | 3·20 | ·0469 |
| 7·20 | ·0303 | 5·00 | ·0323 | 5·05 | ·0351 | 4·13 | ·0429 | 3·82 | ·0462 |
| 9·10 | ·0299 | 5·97 | ·0323 | 6·17 | ·0349 | 5·02 | ·0429 | 4·65 | ·0462 |
| 12·50 | ·0301 | 7·38 | ·0324 | 7·88 | ·0349 | 6·42 | ·0429 | 5·90 | ·0464 |
| 20·25 | ·0301 | 9·74 | ·0323 | (2) 28·83* | ·0348 | 8·91 | ·0428 | 8·18 | ·0462 |
| | | 14·35 | ·0322 | 55·62 | ·0355 | 14·70 | ·0427 | 13·32 | ·0464 |
| | | 27·41 | ·0323 | | | 47·24 | ·0430 | 41·28 | ·0466 |
| Mean rate ·0301 | | Mean rate ·0323 | | Mean rate ·0350 | | Mean rate ·0429 | | Mean rate ·0465 | |

| $n = 17$,<br>$y_0 = 11·22$. | | $n = 18$,<br>$y_0 = 11·29$. | | $n = 20$,<br>$y_0 = 5·11$. | | $n = 25$,<br>$y_0 = 5·09$. | | $n = 30$,<br>$y_0 = 5·06$. | |
|---|---|---|---|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 1′·92 | ·0486 | 1′·83 | ·0507 | 3′·67 | ·0592 | 2′·83 | ·0773 | 2′·31 | ·0951 |
| 2·10 | ·0490 | 1·95 | ·0525 | 4·75 | ·0586 | 3·67 | ·0762 | 2·98 | ·0948 |
| 2·31 | ·0497 | (2) 4·32 | ·0561 | 6·58 | ·0589 | 5·05 | ·0774 | 4·15 | ·0953 |
| 2·62 | ·0495 | 2·77 | ·0533 | 11·03 | ·0582 | 8·45 | ·0769 | 7·01 | ·0946 |
| 3·00 | ·0497 | 3·25 | ·0532 | 39·50 | ·0585 | | | 30·38 | ·0951 |
| 3·53 | ·0495 | 3·91 | ·0536 | | | | | | |
| 4·27 | ·0498 | 4·99 | ·0531 | | | | | | |
| 5·47 | ·0494 | 6·83 | ·0531 | | | | | | |
| 7·50 | ·0495 | 10·70 | ·0537 | | | | | | |
| 12·26 | ·0489 | 28·58 | ·0522 | | | | | | |
| 34·80 | ·0492 | | | | | | | | |
| Mean rate ·0493 | | Mean rate ·0531 | | Mean rate ·0587 | | Mean rate ·0769 | | Mean rate ·0950 | |

It will be seen that approximately from $n = 5$ to $n = 12$ the values of $\alpha$ increase in arithmetical progression with a mean difference of ·00252; from $n = 15$ to $n = 20$ the values of $\alpha$ increase in arithmetical progression with a mean difference of ·00313; and from $n = 20$ to $n = 30$ the values of $\alpha$ increase in arithmetical progression with

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* "(2)" prefixed to an interval means that, an observation having been missed, the interval is that in which two units of change occurred.

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a mean difference of ·00363. The most probable values of $\alpha$ calculated on the hypothesis that there are three such series, are given in Table II., the three formulæ being

$$\alpha = \cdot00250\, n + \cdot0047 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

$$\alpha = \cdot00312\, n - \cdot0037 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

$$\alpha = \cdot00367\, n - \cdot0147 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

TABLE II.

| $n$. | $\alpha$. | | Differences $(\alpha' - \alpha)/(n' - n)$. | |
|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. |
| 5 | ·0175 | ·0172 | | |
| 6 | ·0200 | ·0197 | ·0025 | ·0025 |
| 7 | ·0222 | ·0222 | ·0022 | ·0025 |
| 8 | ·0245 | ·0247 | ·0023 | ·0025 |
| 9 | ·0270 | ·0272 | ·0025 | ·0025 |
| 10 | ·0301 | ·0297 | ·0031 | ·0025 |
| 11 | ·0323 | ·0322 | ·0022 | ·0025 |
| 12 | ·0350 | ·0347 | ·0027 | ·0025 |
| 13·5 | | ·0384 | | ·0025 |
| 13·5 | | ·0384 | | |
| 15 | ·0429 | ·0431 | | ·0031 |
| 16 | ·0465 | ·0462 | ·0036 | ·0031 |
| 17 | ·0493 | ·0493 | ·0028 | ·0031 |
| 18 | ·0531 | ·0525 | ·0038 | ·0032 |
| 20 | ·0587 | ·0587 | ·0028 | ·0031 |
| 20 | ·0587 | ·0587 | | |
| 25 | ·0769 | ·0770 | ·0036 | ·0037 |
| 30 | ·0950 | ·0954 | ·0036 | ·0037 |

In other sets of observations on the effects of varying the mass of hydrogen sulphate, and of other substances, in unit volume, the amounts of potassium iodide have been different, and sometimes hydrogen iodide or sodium iodide has been used instead of potassium iodide. For the comparison of the rates it is convenient to reduce them in all cases to what they would have been with an unit of iodide of whatever kind.

If $i$ denotes the number of millionth-gram molecules of iodide and $s$ the number of millionth-gram molecules of hydrogen sulphate in a cub. centim., the three formulæ become,

$$\alpha = i\,\{4730 + 18\,(s - 190\cdot5)\}\; 10^{-6} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4),$$

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$$\alpha = i\,\{10550 + 22{\cdot}5\,(s - 514)\}\,10^{-6} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5),$$

$$\alpha = i\,\{16130 + 26{\cdot}5\,(s - 762)\}\,10^{-6} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6).$$

(4) expresses the relation from $s = 190$ to $s = 514$; (5) from $s = 514$ to $s = 762$; (6) from $s = 762$ to $s = 1143$.

In these equations, and the corresponding equations which follow, the three constants have the following significance. Taking (4) as an example, the number 4730 depends on the nature of the reacting substances and on the temperature of the solution, it may also vary with the value of $i$ (as is shown subsequently, p. 842) but not with the value of $s$. The number 18 also depends on the nature of the reacting substances and the temperature, but not on the values of $i$ or $s$; it is the increment of rate with a millionth-gram molecule of iodide per cub. centim. due to each additional millionth-gram molecule of hydrogen sulphate. The number 190·5 is the minimum number of such molecules of hydrogen sulphate taken in any experiment of this series. It appears therefore that the increment in the rate of change due to each unit-substitution of sulphuric acid for water is constant till a certain ratio of acid to water is reached; at this point the increment suddenly rises and remains constant until another ratio of acid to water is reached, after which it again rises and then remains constant as far as our experiments proceeded.

In the most dilute solution, where $s = 190$, the number of water-molecules for every molecule of hydrogen sulphate was 289; where the increment of the rate first changes, at $s = 514$, the number of water-molecules was 106; where the second change occurs, at $s = 762$, it was 71, and in the last experiment it was 46.

These results, which are confirmed by two subsequent sets of observations, accord with a view which seems on other grounds to be probable, and which may be stated as follows. When a drop of sulphuric acid is mixed with a relatively large volume, such as 500 cub. centims. of water, the liquid consists of a mixture of water with whatever hydrate of the acid contains the largest number of molecules of water. If the addition of acid is continued slowly drop by drop, each drop increases the proportion of this first hydrate and diminishes the proportion of water, till a point is reached at which the liquid consists of the hydrate. After this point, a new order of events begins; a second hydrate is formed with a larger proportion of acid, its amount increasing and that of the first hydrate decreasing, till the liquid consists of the second hydrate; then begins the formation of a third hydrate, and so on. Thus, the change would proceed regularly, but discontinuously, through a number of successive hydrates, each gradually replacing its predecessor, till finally the liquid consisted of a mixture of the $n^{\text{th}}$ hydrate, having the minimum proportion of water, with sulphuric acid. The influence of such hydrates upon the rate of a chemical change occurring in their presence may probably not be exactly in proportion to the ratio of acid to water in their composition. If so, when in our experiments, the amount of water or of one hydrate was decreased and that of another hydrate was

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increased in a regular arithmetical progression, it was to be expected that the successive rates would also increase in arithmetical progression, with an increment dependent upon the relative influence of the hydrate that was diminished in quantity and of that which was increased. So where a third hydrate was progressively replacing the second; but the increment of the rate due to the replacement of $H^2SO^4$, $m$ $H^2O$, by $H^2SO^4$, $n$ $H^2O$, might differ from that due to the replacement of $H^2SO^4$, $n$ $H^2O$, by $H^2SO^4$, $p$ $H^2O$.

It will be seen that our experimental results accord with this hypothesis, and are inconsistent with the view that the gradual addition of sulphuric acid to water causes a continuous change in the composition of the liquid.

A second set of observations, made at a lower temperature, the conditions and results of which are given in Table III., shows that the value of the increment of rate, caused by successive replacements of water by hydrogen sulphate, changes abruptly at certain points. The position of these points, as of those assumed in the previous set of experiments, cannot be exactly determined. Small changes in the origin and inclination of the straight lines shown on Diagram 1, which are consistent with the position of the experimental points, materially alter the positions of the intersections. Thus, the existence of two hydrates is much more nearly established than their composition. It is, however, interesting to find that our results are perfectly consistent with the supposition that at the three temperatures at which we have experimented, 16°, 20°, and 30°, the composition of the two hydrates is the same. Their composition is probably not far removed from $H^2SO^4$, 106 $H^2O$, and $H^2SO^4$, 71 $H^2O$, and it may have some significance that these numbers are to one another in the ratio of 3 to 2.

## TABLE III.

$54{\cdot}5nH^2SO^4$, $12{\cdot}2\ HI$, $(55500 - 93n)H^2O$. Temperature 16° C.

| $n = 1$, $y_0 = 14{\cdot}02$. | | $n = 2$, $y_0 = 6{\cdot}5$. | | $n = 2$, $y_0 = 6{\cdot}24$. | | $n = 3$, $y_0 = 6{\cdot}55$. | | $n = 4$, $y_0 = 6{\cdot}39$. | |
|---|---|---|---|---|---|---|---|---|---|
| Intervals. | $a$. | Intervals. | $a$. | Intervals. | $a$. | Intervals. | $a$. | Intervals. | $a$. |
| 6′·68 | ·0111 | 10′·57 | ·0158 | 11′·13 | ·0157 | 8′·27 | ·0200 | 6′·83 | ·0249 |
| 7·20 | ·0111 | 12·77 | ·0157 | 13·58 | ·0156 | 9·95 | ·0200 | 8·32 | ·0247 |
| 7·83 | ·0111 | 16·02 | ·0157 | 17·38 | ·0155 | 12·40 | ·0200 | 10·43 | ·0248 |
| 8·57 | ·0111 | 21·38 | ·0157 | 23·65 | ·0156 | 16·67 | ·0198 | 14·15 | ·0247 |
| 9·47 | ·0111 | 32·45 | ·0157 | 38·20 | ·0155 | 25·07 | ·0198 | 22·05 | ·0246 |
| 10·57 | ·0111 | | | 106·10 | ·0157 | 51·28 | ·0202 | 51·57 | ·0248 |
| 12·00 | ·0111 | | | | | | | | |
| 13·83 | ·0111 | | | | | | | | |
| 16·23 | ·0112 | | | | | | | | |
| Mean rate | ·0111 | Mean rate | ·0157 | Mean rate | ·0156 | Mean rate | ·0200 | Mean rate | ·0247 |

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## TABLE III.—(continued).

| $n = 6$, $y_0 = 6·4$. | | $n = 6$, $y_0 = 4·77$. | | $n = 8$, $y_0 = 6·4$. | | $n = 8$, $y_0 = 6·15$. | | $n = 10$, $y_0 = 6·45$. | |
|---|---|---|---|---|---|---|---|---|---|
| Intervals. | α. | Intervals. | α. | Intervals. | α. | Intervals. | α. | Intervals. | α. |
| 4′·98 | ·0341 | 6′·97 | ·0337 | 3′·87 | ·0439 | 4′·11 | ·0433 | 3′·15 | ·0535 |
| 6·02 | ·0340 | 9·12 | ·0338 | 4·68 | ·0438 | 4·94 | ·0437 | 3·80 | ·0532 |
| 7·58 | ·0340 | 13·22 | ·0339 | 5·95 | ·0434 | 6·39 | ·0432 | 4·75 | ·0535 |
| 10·27 | ·0338 | 24·55 | ·0339 | 8·05 | ·0433 | 8·87 | ·0431 | 6·48 | ·0528 |
| 15·73 | ·0342 | | | 12·47 | ·0432 | 14·60 | ·0430 | 9·93 | ·0528 |
| 37·00 | ·0339 | | | 29·00 | ·0433 | 46·96 | ·0433 | 22·00 | ·0532 |
| Mean rate ·0340 | | Mean rate ·0338 | | Mean rate ·0434 | | Mean rate 0·433 | | Mean rate ·0532 | |

| $n = 10$, $y_0 = 6·2$. | | $n = 12$, $y_0 = 6·4$. | | $n = 12$, $y_0 = 6·18$. | | $n = 14$, $y_0 = 6·44$. | | $n = 14$, $y_0 = 6·12$. | |
|---|---|---|---|---|---|---|---|---|---|
| Intervals. | α. | Intervals. | α. | Intervals. | α. | Intervals. | α. | Intervals. | α. |
| 3′·30 | ·0533 | 3′·20 | ·0640 | 3′·32 | ·0644 | 2′·2 | ·0767 | 2′·87 | ·0757 |
| 4·04 | ·0528 | 4·03 | ·0640 | 4·25 | ·0643 | 2·7 | ·0752 | 3·66 | ·0761 |
| 5·11 | ·0532 | 5·42 | ·0643 | 5·88 | ·0641 | 3·35 | ·0762 | 5·11 | ·0757 |
| 7·07 | ·0530 | 8·38 | ·0643 | 9·53 | ·0641 | 4·55 | ·0755 | 8·49 | ·0752 |
| 11·46 | ·0528 | 19·52 | ·0643 | 28·84 | ·0643 | 7·00 | ·0753 | 29·57 | ·0755 |
| 33·79 | ·0531 | | | | | 15·52 | ·0764 | | |
| Mean rate ·0530 | | Mean rate ·0642 | | Mean rate ·0642 | | Mean rate ·0759 | | Mean rate ·0756 | |

| $n = 16$, $y_0 = 6·42$. | | $n = 16$, $y_0 = 6·25$. | | $n = 16$, $y_0 = 7$. | | $n = 17$, $y_0 = 6·28$. | | $n = 18$, $y_0 = 6·5$. | |
|---|---|---|---|---|---|---|---|---|---|
| Intervals. | α. | Intervals. | α. | Intervals. | α. | Intervals. | α. | Intervals. | α. |
| 1′·87 | ·0904 | 1′·93 | ·0902 | 2′·01 | ·0908 | 2′·18 | ·0964 | (2) 4′·43 | ·1021 |
| 2·28 | ·0893 | 2·37 | ·0893 | 2·49 | ·0895 | 2·77 | ·0962 | 3·32 | ·1014 |
| 2·84 | ·0902 | 3·03 | ·0885 | 3·24 | ·0889 | 3·80 | ·0955 | 5·02 | ·1017 |
| 3·87 | ·0893 | 4·23 | ·0869 | 4·48 | ·0906 | 6·07 | ·0951 | 10·74 | ·1023 |
| 5·96 | ·0894 | 6·65 | ·0883 | 7·76 | ·0893 | 15·67 | ·0968 | | |
| 13·57 | ·0894 | 18·13 | ·0887 | | | | | | |
| Mean rate ·0897 | | Mean rate ·0886 | | Mean rate ·0898 | | Mean rate ·0960 | | Mean rate ·1019 | |

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TABLE III.—(continued).

| $n = 18$,<br>$y_0 = 6·35$. | | $n = 18$,<br>$y_0 = 6·23$. | | $n = 18$,<br>$y_0 = 6·98$. | | $n = 20$,<br>$y_0 = 6·53$. | | $n = 20$,<br>$y_0 = 6·29$. | |
|---|---|---|---|---|---|---|---|---|---|
| Intervals. | α. | Intervals. | α. | Intervals. | α. | Intervals. | α | Intervals. | α. |
| ′ | | ′ | | ′ | | ′ | | ′ | |
| 2·02 | ·1026 | 2·08 | ·1017 | 2·17 | ·1035 | 1·72 | ·1161 | 1·77 | ·1184 |
| 2·60 | ·1005 | 2·63 | ·1024 | 2·78 | ·1019 | 2·15 | ·1161 | 2·24 | ·1184 |
| 3·48 | ·1019 | 3·63 | ·1019 | 2·98 | ·1030 | 2·85 | ·1167 | 3·07 | ·1180 |
| 5·48 | ·1012 | 5·85 | ·1014 | 6·90 | ·1019 | 13·48 | ·1156 | 4·88 | ·1186 |
| 13·17 | ·1023 | 16·33 | ·1014 | | | | | 12·70 | ·1184 |
| Mean rate ·1017 | | Mean rate ·1018 | | Mean rate ·1025 | | Mean rate ·1161 | | Mean rate ·1183 | |

It will be seen that approximately from $n = 1$ to $n = 8$ the values of $\alpha$ are in arithmetical progression with a mean difference ·0046, from $n = 10$ to $n = 14$ the values of $\alpha$ are in arithmetical progression with a mean difference ·0056, and from $n = 14$ to $n = 20$ the values of $\alpha$ are in arithmetical progression with a mean difference of ·0068. The most probable values of $\alpha$ calculated on this hypothesis are given in the third column of Table IV., the formulæ from $n = 1$ to $n = 8$, from $n = 10$ to $n = 14$, and from $n = 14$ to $n = 20$, being severally,

$$\alpha = \cdot 0046\, n + \cdot 0064 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7),$$

$$\alpha = \cdot 0057\, n - \cdot 004 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8),$$

$$\alpha = \cdot 0067\, n - \cdot 0180 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9).$$

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## TABLE IV.

| $n$. | $\alpha$. | | Differences $(\alpha' - \alpha)/(n' - n)$. | |
|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. |
| 1 | ·0111 | ·0110 | | |
| 2 | ·0156 | ·0156 | ·0045 | ·0046 |
| 3 | ·0200 | ·0202 | ·0044 | ·0046 |
| 4 | ·0247 | ·0248 | ·0047 | ·0046 |
| 6 | ·0339 | ·0340 | ·0046 | ·0046 |
| 8 | ·0433 | ·0432 | ·0047 | ·0046 |
| 9·46 | | ·0499 | | ·0046 |
| 9·46 | | ·0499 | | |
| 10 | ·0531 | ·0530 | | ·0057 |
| 12 | ·0642 | ·0644 | ·0055 | ·0057 |
| 14 | ·0757 | ·0758 | ·0057 | ·0057 |
| 14 | ·0757 | ·0758 | | |
| 16 | ·0894 | ·0892 | ·0067 | ·0067 |
| 17 | ·0960 | ·0959 | ·0069 | ·0067 |
| 18 | ·1020 | ·1026 | ·0060 | ·0067 |
| 20 | ·1172 | ·1160 | ·0076 | ·0067 |

If $i$ and $s$ denote the number of $HI$ and $H^2SO^4$ in a cubic centimetre, the three formulæ become

$$\alpha = i\,\{902 + 6{\cdot}92\,(s - 54{\cdot}5)\}\,10^{-6} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10),$$

$$\alpha = i\,\{4090 + 8{\cdot}57\,(s - 515)\}\,10^{-6} \quad . \quad . \quad . \quad . \quad . \quad . \quad (11),$$

$$\alpha = i\,\{6210 + 10{\cdot}08\,(s - 763)\}\,10^{-6} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12).$$

(10) expresses the relation from $s = 54$ to $s = 515$, (11) from $s = 515$ to $s = 763$, (12) from $s = 763$ to about $s = 1100$.

If these three equations are compared with the corresponding three, (4), (5), and (6), deduced from the observations with a liquid of higher temperature, it will be seen that the increment in the rate of change due to an unit of hydrogen sulphate undergoes the same abrupt transitions at the same values of $s$, viz., $s = 515$ and 763 in this case, and $s = 514$ and 762 in the former case.

Also the ratios of the corresponding values of the increment per unit of hydrogen sulphate between and above these points are very nearly the same in the two sets, namely, $18 : 6{\cdot}92 = 2{\cdot}61$; $22{\cdot}5 : 8{\cdot}57 = 2{\cdot}62$; $26{\cdot}5 : 10{\cdot}08 = 2{\cdot}63$; the mean ratio being 2·62. Thus a rise of temperature of 14° augments in all three cases the increment of the rate of change per unit of hydrogen sulphate in the ratio 2·62 : 1.

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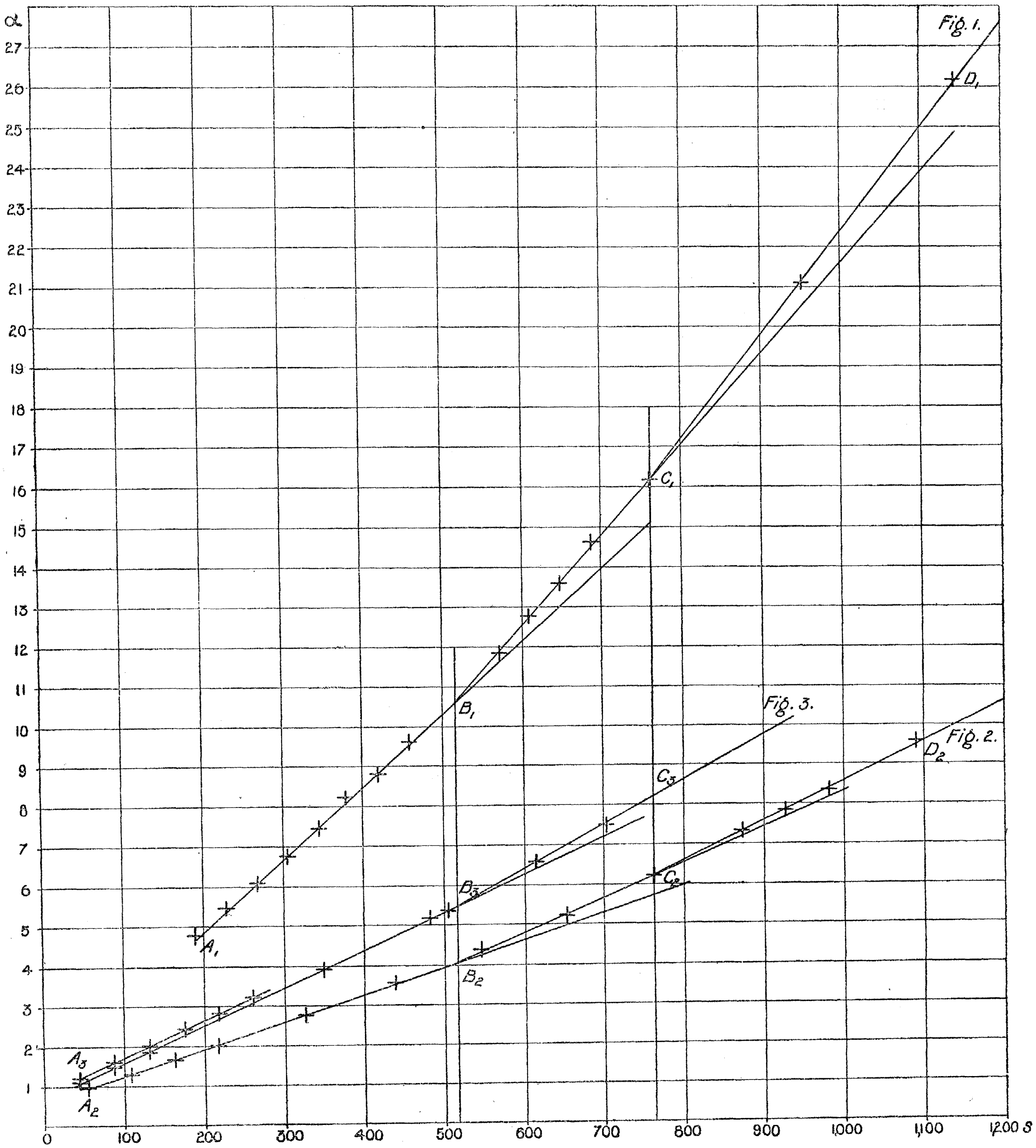
This result will be found to agree absolutely with the ratio deduced from experiments on the effect of increase of temperature upon the rate of change (p. 868), according to which the ratio should be $\left(\frac{273 + 30}{273 + 16}\right)^{20 \cdot 38} = 2{\cdot}62$.

Diagram 1.



On Diagram 1, figs. 1, 2, and 3, the units of hydrogen sulphate are measured along the horizontal axis and the units of actual change per thousand of potential change,

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per minute, along the vertical axis. The ordinate at each point is found by dividing the experimental rate by the number of units of iodide and, for convenience of scale, multiplying by one thousand. The lines are those expressed by the equations (4), (5), (6), &c., multiplied by $1000/i$. For example, the position of the point $D_1$ denotes that in a solution of the temperature 30°, containing per cubic centim. $HI$ and 1143 $H^2SO^4$ and a constant amount of hydrogen dioxide corresponding to 1000 units of potential change, the number of units of actual change in one minute would be 26·1. The line $A_1B_1$ is that expressed by the equation $\alpha = \{4730 + 18\,(s - 190{\cdot}5)\}\,10^{-3}$, the ordinate of the lowest point of which, when $s = 190{\cdot}5$, is 4·73. It will be seen that the straight lines $A_1B_1$, $B_1C_1$, $C_1D_1$, and the corresponding lines in figs. 2 and 3, pass very close to the experimental points and that no continuous curve would pass as near these points. Of these lines, $A_1B_1$ represents the law of variation of the rate of change with hydrogen sulphate when the units of the latter vary between 190 and 514, $B_1C_1$ when the units vary between 514 and 762, $C_1D_1$ when the units vary between 762 and 1143. Similarly $A_2B_2$ represents the law of variation of the rate of change at 16° when the units of hydrogen sulphate vary from 54 to 515, $B_2C_2$ when the units vary from 515 to 763, $C_2D_2$ when the units vary from 763 to 981. The points of abrupt transition of value of the increment of the rate of change per unit of hydrogen sulphate are in the one case $B_1$ and $C_1$; in the other $B_2$ and $C_2$.

As the intervals to be observed in the last three or four sets of the series at 16° C. (Tables III. and IV.) were rather short for accurate determination, the sets were repeated with one-third the amount of hydrogen iodide previously used. The conditions and results are given in the following Table :—

TABLE V.

$54{\cdot}5\ n\ H^2SO^4$, $4{\cdot}07\ HI$, $(55500 - 93\ n)\ H^2O$. Temperature 16° C.

| $n = 14$,<br>$y_0 = 7{\cdot}14$. | | $n = 16$,<br>$y_0 = 7{\cdot}01$. | | $n = 18$,<br>$y_0 = 7{\cdot}1$. | | $n = 20$.<br>$y_0 = 7{\cdot}01$. | |
|---|---|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| ′<br>5·96 | ·0253 | ′<br>5·16 | ·0298 | ′<br>4·43 | ·0343 | ′<br>3·88 | ·0396 |
| 7·07 | ·0252 | 6·14 | ·0297 | 5·27 | ·0340 | 4·64 | ·0393 |
| 8·62 | ·0251 | 7·59 | ·0293 | 6·34 | ·0344 | 5·72 | ·0389 |
| 11·02 | ·0251 | 9·67 | ·0297 | 8·19 | ·0341 | 7·36 | ·0389 |
| 15·20 | ·0252 | 13·62 | ·0297 | 11·44 | ·0340 | 10·40 | ·0388 |
| 25·01 | ·0252 | 23·18 | ·0297 | 19·05 | ·0339 | 17·62 | ·0390 |
| | | | | 70·31 | ·0341 | | |
| Mean rate . | ·0252 | Mean rate . | ·0297 | Mean rate . | ·0341 | Mean rate . | ·0391 |

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Comparing the rates in this and the previous series, it is seen that they agree, the effect of reducing the amount of iodide to one-third being to reduce the rate in the same proportion. With 14, 16, 18, and 20 proportions of hydrogen sulphate the rates are,

| | | | | |
|---|---|---|---|---|
| in the first case . . . . . . . | ·0757, | ·0894, | ·1020, | ·1172; |
| in the second case . . . . . . | ·0252, | ·0297, | ·0341, | ·0391. |
| The top row, divided by 3, become | ·0252, | ·0298, | ·0340, | ·0391. |

Table VI. gives the conditions and results of a fourth series of experiments, in which smaller proportions of hydrogen sulphate were taken, rates convenient for observation being maintained by using more iodide and a higher temperature.

### TABLE VI.

7·62 $nH^2SO^4$, 14·22 $HI$, (55400 — 15$n$) $H^2O$. Temperature 30° C.

| $n = 0$,<br>$y_0 = 17.$ | | $n = 1$,<br>$y_0 = 17·7.$ | | $n = 2$,<br>$y_0 = 15·65.$ | | $n = 3$,<br>$y_0 = 17·8.$ | | $n = 4$,<br>$y_0 = 17·86.$ | |
|---|---|---|---|---|---|---|---|---|---|
| Intervals. | α. | Intervals. | α. | Intervals. | α. | Intervals. | α. | Intervals. | α. |
| 2·90 | ·0209 | (2) 4·92 | ·0244 | 2·43 | ·0271 | 1·93 | ·0300 | 1·82 | ·0316 |
| 2·97 | ·0217 | 2·71 | ·0243 | 2·63 | ·0269 | 2·07 | ·0296 | 1·90 | ·0320 |
| 3·30 | ·0209 | 2·94 | ·0240 | 2·79 | ·0272 | 2·22 | ·0294 | 2·01 | ·0324 |
| 3·53 | ·0210 | 3·10 | ·0244 | 3·06 | ·0269 | 2·35 | ·0299 | 2·17 | ·0321 |
| 3·82 | ·0209 | 3·40 | ·0242 | 3·32 | ·0270 | 2·56 | ·0294 | 2·30 | ·0318 |
| 4·16 | ·0209 | 3·68 | ·0243 | 3·62 | ·0272 | 2·72 | ·0299 | 2·53 | ·0320 |
| 4·59 | ·0207 | 4·07 | ·0240 | 4·08 | ·0268 | 2·95 | ·0300 | 2·75 | ·0320 |
| 5·08 | ·0207 | 4·52 | ·0242 | 4·58 | ·0269 | 3·33 | ·0292 | 2·99 | ·0323 |
| 5·62 | ·0209 | 5·02 | ·0243 | 5·17 | ·0271 | 3·65 | ·0295 | 3·36 | ·0318 |
| 6·40 | ·0209 | 5·77 | ·0241 | 6·00 | ·0272 | (2) 8·65 | ·0299 | 3·75 | ·0319 |
| 7·26 | ·0212 | 6·71 | ·0240 | 7·20 | ·0270 | 5·45 | ·0292 | 4·27 | ·0319 |
| | | 7·92 | ·0243 | 8·97 | ·0270 | 6·44 | ·0294 | 4·95 | ·0318 |
| | | 9·77 | ·0245 | 11·95 | ·0268 | 7·98 | ·0292 | 5·85 | ·0320 |
| | | 12·91 | ·0244 | 17·41 | ·0272 | 10·17 | ·0301 | 7·18 | ·0321 |
| | | 19·00 | ·0243 | | | 14·63 | ·0302 | 9·40 | ·0319 |
| | | 37·00 | ·0240 | | | 27·12 | ·0299 | 37·17 | ·0324 |
| Mean rate | ·0210 | Mean rate | ·0242 | Mean rate | ·0270 | Mean rate | ·0297 | Mean rate | ·0320 |

The rates are very nearly in arithmetical progression, as the following comparison shows:—

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TABLE VII.

| $n$. | $\alpha$. | $\alpha'$. | Differences, $\alpha_n - \alpha_{n-1}$. | Difference per unit, $HI$ and $H^2SO^4$. |
|---|---|---|---|---|
| 0 | ·0210 | ·0213 | | |
| 1 | ·0242 | ·0241 | ·0032 | ·0000295 |
| 2 | ·0270 | ·0268 | ·0028 | ·0000258 |
| 3 | ·0297 | ·0296 | ·0027 | ·0000249 |
| 4 | ·0320 | ·0323 | ·0023 | ·0000212 |

The rates given under $\alpha'$ are in arithmetical progression, with a difference ·00276. The actual differences, which follow, show however a fall in value which is not likely to be accidental, and may mean that when such small quantities of sulphuric acid are added as 1, 2, 3, 4 molecules to about 7000 molecules of water, the increment of the rate with each addition is nearly constant, but shows a slight decrease. Probably the main effect is a constant increment, but some slight secondary effect of the presence of sulphuric acid, in very dilute solutions, causes a further acceleration, which, with larger quantities, is no longer discernible.

Tables VIII., VIII.A, and IX. give the results of two further series of experiments, in which the rate of change was determined in presence of quantities of sulphuric acid such that the ratio of the number of molecules of water to one molecule of sulphuric acid varied from 830,000, where no sulphuric acid was added beyond the small quantity present in the solution of hydrogen dioxide, to 77. In the first series of experiments the amount of sulphuric acid was increased until the proportion of water molecules was reduced to 209. The earlier experiments of this series are placed in a separate table (VIII.A), and are reserved for subsequent discussion, because in this case also the effect of the first additions of very small quantities of acid differs from that of subsequent additions. The second series (Table IX.) was a continuation of the first, except that the mass of hydrogen iodide per cubic centimetre was reduced from 22·8 to 11·4 $HI$, in order to prevent the rate of change with the larger proportions of sulphuric acid becoming too great for accurate observation.

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TABLE VIII.—(·067 + 43·85$n$) $H^2SO^4$, 22·82 $HI$, (55474 − 81$n$) $H^2O$.
Temperature, 20° C.

| $n = 1$,<br>$y_0 = 8·485$. | | $n = 2$,<br>$y_0 = 8·29$. | | $n = 3$,<br>$y_0 = 8·115$. | |
|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 4′·60 | ·0272 | 3′·50 | ·0367 | 2′·88 | ·0457 |
| 5·27 | ·0272 | 4·00 | ·0369 | 3·28 | ·0461 |
| 6·13 | ·0274 | 4·72 | ·0367 | 3·92 | ·0455 |
| 7·43 | ·0271 | 5·68 | ·0369 | 4·75 | ·0458 |
| 9·27 | ·0272 | 7·20 | ·0368 | 6·07 | ·0458 |
| 12·35 | ·0274 | 9·87 | ·0367 | 8·45 | ·0457 |
| 18·75 | ·0274 | 15·58 | ·0369 | 14·18 | ·0451 |
| 41·00 | ·0272 | 40·63 | ·0367 | 49·93 | ·0455 |
| Mean rate . . | ·0273 | Mean rate . . | ·0368 | Mean rate . . | ·0457 |

| $n = 4$,<br>$y_0 = 8·84$. | | $n = 5$,<br>$y_0 = 8·495$. | | $n = 6$,<br>$y_0 = 6·83$. | |
|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 2′·48 | ·0551 | 1′·97 | ·0636 | 2′·18 | ·0727 |
| 2·87 | ·0551 | 2·23 | ·0642 | 2·57 | ·0732 |
| 3·38 | ·0555 | 2·63 | ·0636 | 3·20 | ·0725 |
| 4·22 | ·0549 | 3·17 | ·0634 | 4·15 | ·0730 |
| 5·43 | ·0555 | 3·95 | ·0637 | 6·00 | ·0727 |
| 7·90 | ·0549 | 5·28 | ·0638 | 10·83 | ·0730 |
| 14·22 | ·0551 | 8·08 | ·0634 | | |
| | | 17·33 | ·0638 | | |
| Mean rate . . | ·0551 | Mean rate . . | ·0637 | Mean rate . . | ·0729 |

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TABLE VIIIA.—$(\cdot 067 + 8\cdot 8n)\,H^2SO^4$, 22·82 *HI*. Temperature 20° C.

| $n = 0$, $y_0 = 8\cdot 88$. | | $n = 1$, $y_0 = 7\cdot 35$. | | $n = 3$, $y_0 = 5\cdot 67$. | |
|---|---|---|---|---|---|
| Intervals. | α. | Intervals. | α. | Intervals. | α. |
| 7′·18 | ·0166 | 7′·40 | ·0198 | 8′·25 | ·0235 |
| 8·13 | ·0167 | 8·70 | ·0197 | 10·30 | ·0234 |
| 9·40 | ·0167 | 10·47 | ·0198 | 13·57 | ·0234 |
| 11·22 | ·0166 | 13·27 | ·0197 | 20·10 | ·0233 |
| 13·77 | ·0166 | 18·02 | ·0196 | 38·98 | ·0234 |
| 17·90 | ·0166 | 28·23 | ·0196 | | |
| 28·60 | ·0167 | 67·13 | ·0201 | | |
| 45·53 | ·0167 | | | | |
| Mean rate . . | ·0167 | Mean rate . . | ·0197 | Mean rate . . | ·0234 |

TABLE IX.—$(\cdot 067 + 43\cdot 85n)\,H^2SO^4$, 11·41 *HI*, $(55537 - 88\cdot 5n)\,H^2O$.
Temperature 20° C.

| $n = 1$, $y_0 = 6\cdot 7$. | | $n = 2$, $y_0 = 5\cdot 95$. | | $n = 3$, $y_0 = 6\cdot 25$. | | $n = 5$, $y_0 = 6\cdot 92$ | |
|---|---|---|---|---|---|---|---|
| Intervals. | α. | Intervals. | α. | Intervals. | α. | Intervals. | α. |
| 12′·72 | ·0127 | 10′·35 | ·0178 | 7′·83 | ·0222 | 4′·87 | ·0321 |
| 15·24 | ·0127 | 12·80 | ·0176 | 9·55 | ·0221 | 5·80 | ·0319 |
| 18·88 | ·0127 | 16·87 | ·0173 | 12·25 | ·0219 | 7·08 | ·0321 |
| 24·89 | ·0127 | 23·68 | ·0175 | 16·73 | ·0220 | 9·28 | ·0318 |
| 36·39 | ·0127 | 40·88 | ·0176 | 26·78 | ·0219 | 13·20 | ·0317 |
| 69·70 | ·0127 | | | 73·70 | ·0218 | 22·98 | ·0320 |
| Mean rate . | ·0127 | Mean rate . | ·0176 | Mean rate . | ·0220 | Mean rate . | ·0319 |

| $n = 8$, $y_0 = 6\cdot 49$. | | $n = 11$, $y_0 = 7\cdot 145$. | | $n = 14$, $y_0 = 5\cdot 86$. | | $n = 16$, $y_0 = 6\cdot 295$. | |
|---|---|---|---|---|---|---|---|
| Intervals. | α. | Intervals. | α. | Intervals. | α. | Intervals. | α. |
| 3′·75 | ·0446 | 2′·57 | ·0587 | 2′·50 | ·0749 | 2′·02 | ·0858 |
| 4·53 | ·0444 | 3·00 | ·0592 | 3·05 | ·0756 | 2·43 | ·0860 |
| 5·68 | ·0444 | 3·67 | ·0588 | 4·02 | ·0747 | 3·13 | ·0848 |
| 7·57 | ·0446 | 4·68 | ·0591 | 5·77 | ·0747 | 4·22 | ·0858 |
| 11·50 | ·0446 | 6·48 | ·0591 | 10·28 | ·0750 | 6·70 | ·0856 |
| 24·83 | ·0448 | 10·68 | ·0590 | | | | |
| | | 35·08 | ·0588 | | | | |
| Mean rate . | ·0446 | Mean rate . | ·0589 | Mean rate . | ·0749 | Mean rate . | ·0856 |

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In the preceding tables the number of millionth-gram molecules of water per cub. centim. was determined by weighing a known volume of the liquid after each set of observations. The total mass thus found, less the masses of the other substances, was the mass of water, and this divided by the volume and by 18, the molecular weight of water, and multiplied by a million, gave the required number. It was found that these numbers decreased very nearly in arithmetical progression with the increase of sulphuric acid, and this relation is assumed in the formulæ $(55474 - 81n)\ H^2O$ at the head of Table VIII., and $(55537 - 88{\cdot}5n)\ H^2O$ at the head of Table IX.

In the following table the results given in Table VIII. are compared with a series in arithmetical progression.

TABLE X.

| $n$. | $\alpha$. | | Differences $(\alpha' - \alpha)/(n' - n)$. | |
|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. |
| 1 | ·0273 | ·0275 | | |
| 2 | ·0368 | ·0366 | ·0095 | ·0091 |
| 3 | ·0457 | ·0457 | ·0089 | ·0091 |
| 4 | ·0551 | ·0548 | ·0094 | ·0091 |
| 5 | ·0637 | ·0639 | ·0086 | ·0091 |
| 6 | ·0729 | ·0730 | ·0092 | ·0091 |

The calculated values of $\alpha$ are deduced from the formula

$$\alpha = {\cdot}01844 + {\cdot}00909n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13),$$

which for $i$ units of iodide and $s$ $H^2SO^4$ in one cub. centim. becomes

$$\alpha = i\,\{1206 + 9{\cdot}08\,(s - 43{\cdot}85)\}10^{-6} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14).$$

This formula is represented graphically on Diagram 1, by the straight line above $A_3B_3$ and parallel to it.

The coefficient of $s$, $9{\cdot}08 \times 10^{-6}$, when multiplied by the factor $\left(\frac{273 + 30}{273 + 20}\right)^{20{\cdot}38}$ which (p. 868, *et seq.*) expresses the effect of an increase of temperature from 20° to 30°, gives $18 \times 10^{-6}$, which according to equation (4) is the coefficient of $s$ for similar concentrations at 30°.

Table XI. gives a comparison of the results shown on Table IX. with two series in arithmetical progression.

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TABLE XI.

| $n$. | $\alpha$. | | Differences $(\alpha' - \alpha)/(n' - n)$. | |
|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. |
| 1 | ·0127 | ·0130 | | |
| 2 | ·0176 | ·0175 | ·0049 | ·0045 |
| 3 | ·0220 | ·0221 | ·0044 | ·0046 |
| 5 | ·0319 | ·0312 | ·0049 | ·0045 |
| 8 | ·0446 | ·0450 | ·0043 | ·0046 |
| 11 | ·0589 | ·0587 | ·0048 | ·0046 |
| 11·75 | .. | ·0621 | .. | ·0045 |
| 11·75 | .. | ·0621 | .. | |
| 14 | ·0749 | ·0748 | .. | ·0056 |
| 16 | ·0856 | ·0861 | ·0053 | ·0056 |

The calculated values of $\alpha$ between $n = 1$ and $n = 11·75$, and between $n = 11·75$ and $n = 16$ are deduced from the equations

$$\alpha = ·01297 + ·00457\,(n - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15),$$

$$\alpha = ·0621 + ·00564\,(n - 11·75) \quad . \quad . \quad . \quad . \quad . \quad . \quad (16).$$

The value of $\alpha$ common to these two formulæ is ·0621, which corresponds to $n = 11·75$, or $s = 515$ (represented by the point $B_3$ in Diagram 1, fig. 3), and to the hydrate, $H^2SO^4$, 106 $H^2O$.

Stated for millionth-gram molecules of iodide and hydrogen sulphate the formulæ become

$$\alpha = i\,\{1139 + 9·13\,(s - 43·85)\}\,10^{-6} \quad . \quad . \quad . \quad . \quad . \quad (17),$$

$$\alpha = i\,\{5440 + 11·27\,(s - 515)\}\,10^{-6} \quad . \quad . \quad . \quad . \quad . \quad (18).$$

These formulæ are represented by the straight lines $A_3B_3$, $B_3C_3$, fig. 3, Diagram 1.

The coefficient of $s$ in (17), namely 9·13, agrees closely with the coefficient of $s$ in (14) which is 9·08. The ratios of the coefficients of $s$ in (17) and in the corresponding formula (4) for the series at 30° is 1·97, and the ratio of the coefficients of $s$ in (18) and in (5) is 1·98. The ratio for a change of temperature from 20° to 30° given by the formula $\left(\frac{273 + 30}{273 + 20}\right)^{20·38}$ is 1·98. Similarly, a comparison of the coefficients of $s$ in (17) and (18) with the corresponding values at 16° in (10) and (11) gives the ratios

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1·32 and 1·315, agreeing in both cases with the ratio calculated from the temperature formula $\left(\frac{273 + 20}{273 + 16}\right)^{20\cdot38} = 1\cdot32$.

There has still to be considered the effect of the small quantities of hydrogen sulphate in the presence of which the observations were made of which the details have been given in Table VIIIA. Their results may be summarized as follows:—

## Table XII.

| $n$. | $\alpha$. | Differences $(\alpha' - \alpha)/(n' - n)$. |
|---|---|---|
| 0 | ·0167 | |
| 1 | ·0197 | ·0030 |
| 3 | ·0234 | ·0018 |

The increment of rate between the first pair of determinations, due to an addition of 8·8 $H^2SO^4$ per cub. centim., and the corresponding diminution of water, is ·003, giving for the increment per unit, or coefficient of $s$, $14\cdot9 \times 10^{-6}$. A comparison of these results with those obtained with similarly small proportions of hydrogen sulphate (Table VII.) shows that both at 20° and at 30° the first small addition of hydrogen sulphate causes a much greater increment of the rate than subsequent small additions, the actual coefficient of $s$ for values of $s$ between 0 and 7·62 being at 30° $29\cdot5 \times 10^{-6}$, which, multiplied by the temperature-factor $\left(\frac{273 + 20}{273 + 30}\right)^{20\cdot38}$ gives the same number as the observations at 20°, namely, $14\cdot9 \times 10^{-6}$.

The coefficient of $s$ between the values of $s$ 8·9 and 26·5, is scarcely higher than it is over the range of values of $s$ from 43·8 to 515 (see equation (15) and line $A_3B_3$, Diagram 1). At 30° the minimum and first constant value of the coefficient of $s$ appears only to be reached when the proportion of acid is rather larger. More experiments with such very dilute solutions at different temperatures would probably yield interesting results.

### *Variation of Hydrogen Chloride.*

The influence of hydrogen chloride upon the rate of change was next investigated. In Table XIII. are recorded the conditions and the rates of change found in a series of sets of observations in which the number of $HCl$ per cub. centim. were varied from 0 to 355.

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## TABLE XIII.

71·1 $n\ HCl$, 14·22 $HI$. Temperature, 30° C.

| $n$ = 0,<br>$y_0$ = 7·51. | | $n$ = 0,<br>$y_0$ = 6·73. | | $n$ = 1,<br>$y_0$ = 7·41. | | $n$ = 2,<br>$y_0$ = 6·11. | |
|---|---|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 6′·90 | ·0207 | (2) 16′·53 | ·0213 | 3′·65 | ·0397 | 3′·85 | ·0567 |
| 7·90 | ·0211 | (2) 26·57 | ·0215 | 4·30 | ·0395 | 4·93 | ·0567 |
| 9·60 | ·0208 | 21·22 | ·0215 | 5·18 | ·0395 | 6·85 | ·0565 |
| 12·18 | ·0206 | 40·30 | ·0214 | 6·55 | ·0393 | 11·47 | ·0559 |
| 16·23 | ·0207 | | | 8·80 | ·0395 | | |
| (2) 76·60 | ·0208 | | | 13·37 | ·0401 | | |
| | | | | 31·37 | ·0394 | | |
| Mean rate . | ·0208 | Mean rate . | ·0214 | Mean rate . | ·0396 | Mean rate . | ·0564 |

| $n$ = 3,<br>$y_0$ = 6·3. | | $n$ = 4,<br>$y_0$ = 6·45. | | $n$ = 4,<br>$y_0$ = 7·72. | | $n$ = 5,<br>$y_0$ = 5·78. | |
|---|---|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 2′·35 | ·0735 | 1′·88 | ·0895 | 1′·50 | ·0925 | (2) 6′·79 | ·108 |
| 2·81 | ·0743 | 2·21 | ·0916 | 1·78 | ·0906 | 4·17 | ·107 |
| 3·63 | ·0730 | 2·70 | ·0946 | 2·12 | ·0906 | 7·67 | ·107 |
| 4·91 | ·0736 | 3·80 | ·0906 | 2·58 | ·0923 | | |
| 7·61 | ·0750 | 5·75 | ·0912 | 3·43 | ·0914 | | |
| 19·85 | ·0738 | 12·95 | ·0904 | 5·03 | ·0912 | | |
| | | | | 9·60 | ·0908 | | |
| Mean rate . | ·0739 | Mean rate . | ·0913 | Mean rate . | ·0913 | Mean rate . | ·1073 |

On Table XIV. the series of rates thus found are compared with numbers calculated on the hypothesis that the increase of rate is proportional to the increase of acid, from the formula

$$\alpha = {\cdot}0397 + {\cdot}017\,(n - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19).$$

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## Table XIV.

| $n$. | $\alpha$. | | Differences $(\alpha' - \alpha)/(n' - n)$. | |
|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. |
| 0 | ·0211 | | | |
| 1 | ·0396 | ·0397 | ·0185 | |
| 2 | ·0564 | ·0567 | ·0168 | ·0170 |
| 3 | ·0739 | ·0737 | ·0175 | ·0170 |
| 4 | ·0913 | ·0907 | ·0174 | ·0170 |
| 5 | ·1073 | ·1077 | ·0160 | ·0170 |

Putting $i$ for the number of $HI$ and $c$ for the number of $HCl$ per cub. centim. the equation which represents the variation of the rate with the amount of hydrogen chloride over the range of these observations is

$$\alpha = i\{2800 + 16{\cdot}8\,(c - 71{\cdot}1)\}10^{-6} \quad . \quad . \quad . \quad . \quad . \quad . \quad (20).$$

The increment of rate per unit of hydrogen chloride between 0 and 71, or up to 0·071 normal, is, as with hydrogen sulphate, greater than that due to subsequent additions of acid which were extended up to 355 $HCl$ per cub. centim. or 0·355 normal. Probably if the rates of change were determined with quantities of hydrogen chloride between 0 and 71 $HCl$ it would be found that only the first ten or twenty millionth-gram molecules per cub. centim. caused a greater acceleration, and that after this point, which may be that at which hydrogen chloride combines with the maximum quantity of water, the acceleration increases in the same ratio as with the subsequent additions of acid. Whether in more concentrated solutions the acceleration due to an increment of hydrogen chloride changes at certain points, as the total amount present and its ratio to the amount of water increases, we have not at present investigated.

Comparing the influence upon the rate of the presence of hydrogen sulphate and of hydrogen chloride respectively, it will be seen that, molecule for molecule, the two acids are nearly equivalent, instead of one molecule of hydrogen sulphate being equivalent to two molecules of hydrogen chloride as in combination with bases In a solution at 30° containing in each cub. centim., besides water, 300 $H^2SO^4$, 4 $HI$, and 1 $H^2O^2$, all these quantities being kept constant, iodine would be formed at the rate of ·0268 $I^2$ per cub. centim. per minute. This amount would be increased to ·034 $I^2$ by bringing into the liquid another 100 $H^2SO^4$ per cub. centim., the increment for each $H^2SO^4$ in presence of 4 $HI$ being over this range of concentration $72 \times 10^{-6}$ (equation 4); it would be increased to ·0335 $I^2$ by adding in each cub. centim. 100 $HCl$, the increment for each $HCl$ in presence of 4 $HI$ being $67{\cdot}2 \times 10^{-6}$ (equation 20).

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### *Variation of Iodide.*

In our former paper on the same subject ('Phil. Trans.,' 1867, pp. 132–135), an account is given of experiments which prove that the rate at which the change under investigation proceeds, varies directly with the amount of iodide, when relatively small quantities of potassium iodide are present in solutions containing relatively large quantities of hydrogen sulphate or hydrogen chloride. It is also pointed out that this relation cannot hold good exactly unless the iodide added has no secondary effect upon the rate of change. Doubtless, every substance in the liquid influences the rate of change, whether itself capable of undergoing change as the reaction proceeds or not. Water promotes the change as little as any other substance with which we have experimented, for the rate of change is generally increased and never decreased by the substitution in a given volume of any of these substances for water. Thus an addition (or substitution for water) of hydrogen iodide, like an addition of hydrogen chloride or hydrogen sulphate, causes an increment in the rate.

The equation $\alpha = \alpha_1 + ak$ gives the rate of change when, $\alpha_1$ being the rate under any fixed conditions, those conditions have been varied by bringing into the solution $a$ units of a substance, one unit of which causes the increment, or additional rate, $k$. With different quantities of hydrogen sulphate, or of hydrogen chloride, and different small quantities of potassium or sodium iodide, the equation takes the form $\alpha = i\,(\alpha_1 + sk)$, or $\alpha = i\,(\alpha_1 + ck)$, and similarly with different quantities of hydrogen iodide or, in presence of sodium hydrogen carbonate, of potassium or sodium iodide, the equation becomes $\alpha = i\,(\alpha_1 + ik)$.

When, however, the variation made in a set of observations is of a neutral iodide in an acid solution, in which the result is the replacement of a small proportion of hydrogen sulphate or chloride by hydrogen iodide and the addition of a small quantity of a neutral salt, the quantity $ik$ becomes so small relatively to $\alpha_1$ as to be negligible, and the equation is simplified to $\alpha = i\alpha_1$.

To illustrate the simple relation which is found to exist in such a case between the amount of iodide and the rate, we reproduce the results of one series of experiments given in our previous paper.

The amounts of potassium iodide taken were, it will be seen, in arithmetical progression from 1·82 $KI$ to eight times that quantity. The corresponding rates are also in arithmetical progression, as is shown by comparing them with numbers calculated from the equation $\alpha = {\cdot}01347n$.

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### TABLE XV.

$(381 \cdot 3 - 1 \cdot 82z)\ HCl$, $1 \cdot 82\ \{(n-z)\ KI + zHI\}$, $1 \cdot 82zKCl$. Temperature, 30° C.

| $n$. | $\alpha$. | |
|---|---|---|
| | Found. | Calculated. |
| 1 | ·0136 | ·0135 |
| 2 | ·0268 | ·0269 |
| 3 | ·0404 | ·0404 |
| 4 | ·0538 | ·0539 |
| 5 | ·0672 | ·0673 |
| 6 | ·0804 | ·0808 |
| 7 | ·0948 | ·0943 |
| 8 | ·1080 | ·1078 |

The equation which gives the rate per unit of iodide is $\alpha = \cdot 0074i$. The maximum variation in the *conditions* of the change, as distinct from the variation of iodide, was, when $n = 8$, the substitution per cub. centim. of 14·6 out of 380 $HCl$ by 14·6 $HI$ and the addition of 14·6$KCl$. Such a change of conditions does not produce a measurable effect.

The following experiment, which gives a similar result, was made in a different manner. The amount of iodide was gradually increased during a set of observations by adding to the liquid single drops of a strong solution of sodium iodide. When three or four observations, giving two or three intervals, had been made, another drop of iodide was brought in; the following interval was occupied with mixing the liquid and adjusting the temperature, and the moment of the next observation of the change of colour was the starting point of the short series of observations which served to determine the rate of change with the new proportion of iodide. In the following Table $n$ represents the number of drops thus added.

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TABLE XVI.

546 $H^2SO^4$, ·266$n$ $NaI$. Temperature, 16° C.

| $n$. | $\alpha$. | | $\alpha/n$. | |
|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. |
| 1 | ·00121 | ·00118 | ·00121 | ·00118 |
| 2 | ·00241 | ·00236 | ·00120 | ” |
| 3 | ·00358 | ·00354 | ·00119 | ” |
| 4 | ·00474 | ·00472 | ·00118 | ” |
| 5 | ·00592 | ·00590 | ·00118 | ” |
| 6 | ·00711 | ·00708 | ·00118 | ” |
| 7 | ·00825 | ·00826 | ·00118 | ” |
| 8 | ·00944 | ·00944 | ·00118 | ” |
| 10 | ·01180 | ·01180 | ·00118 | ” |
| 12 | ·01413 | ·01416 | ·00118 | ” |
| 16 | ·01880 | ·01888 | ·00117 | ” |
| 28 | ·03250 | ·03304 | ·00116 | ” |

It will be seen that the rates vary directly with the amounts of iodide, the numbers in the third column being calculated from the equation $\alpha = \cdot 00118n$, or, per unit of iodide, $\alpha = \cdot 00444i$.

When, however, hydrogen iodide is taken instead of potassium iodide, and in larger quantities, the effect of this acid can be determined like the corresponding effects of hydrogen sulphate and of hydrogen chloride, the second term of the equation $\alpha = i\,(\alpha_1 + ik)$ becoming easily measurable.

In the set of observations whose conditions and results are given in the following table, the amount of hydrogen iodide in each cub. centim. was varied from 14·5 to 43·5 $HI$.

TABLE XVII.

7·25$n$ $HI$. Temperature, 30° C.

| $n = 2$.<br>$y_0 = 7{\cdot}75$. | | $n = 3$.<br>$y_0 = 7{\cdot}95$. | | $n = 4$.<br>$y_0 = 8{\cdot}41$. | | $n = 5$.<br>$y_0 = 7{\cdot}73$. | | $n = 6$.<br>$y_0 = 7{\cdot}7$. | |
|---|---|---|---|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 6′·45 | ·0214 | 3′·90 | ·0344 | 2′·47 | ·0513 | 2′·00 | ·0692 | 1′·57 | ·0879 |
| 7·52 | ·0214 | 4·43 | ·0351 | 2·88 | ·0502 | 2·35 | ·0684 | 1·82 | ·0881 |
| 8·93 | ·0214 | 5·32 | ·0345 | 3·38 | ·0502 | 2·82 | ·0681 | 2·17 | ·0881 |
| 11·05 | ·0214 | 6·47 | ·0348 | 3·95 | ·0516 | 3·50 | ·0678 | 2·68 | ·0881 |
| 14·45 | ·0214 | 8·38 | ·0348 | 5·05 | ·0509 | 4·53 | ·0689 | 3·51 | ·0883 |
| 21·30 | ·0212 | 11·85 | ·0349 | 6·83 | ·0508 | 6·67 | ·0684 | 5·12 | ·0883 |
| | | 20·60 | ·0349 | 10·53 | ·0509 | 12·52 | ·0689 | 9·62 | ·0881 |
| | | | | 24·17 | ·0509 | | | | |
| Mean rate | ·0214 | Mean rate | ·0348 | Mean rate | ·0508 | Mean rate | ·0685 | Mean rate | ·0881 |

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Comparing the rates thus found, it is evident that they are not in arithmetical progression; but such a series of rates is deducible from the equation $\alpha = i(\alpha_1 + ik)$, where $\alpha_1$ represents what the rate would be with an unit of iodide, if the iodide were only a substance capable of undergoing change, and $k$ represents the addition to this rate which is caused by the first and each additional $HI$ per cubic centimetre as an ingredient of the solution promoting the change. The best value for $\alpha_1$ in this case is found to be ·00118, and that for $k$ ·0000194. The values of $\alpha$ in the following table are calculated accordingly from an equation

$$\alpha = n\,({\cdot}00856 + {\cdot}00102\,n) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (21),$$

which, since $n = 7{\cdot}25\,i$, becomes for an unit of iodide

$$\alpha = i\,(1180 + 19{\cdot}4\,i)\,10^{-6} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (22).$$

If that part of the increase of rate which is due to hydrogen iodide being one of the substances undergoing change, and which is therefore directly proportional to the amount of iodide in the liquid, is separated from the other part by reducing all the rates to what they would have been with only one proportion of iodide so acting, the effect of hydrogen iodide as an accelerant will be, so to say, isolated. In the fourth column are given the rates divided by the corresponding proportions of iodide. These numbers are in arithmetical progression and correspond to the previous series representing the accelerating effects of hydrogen sulphate and hydrogen chloride.

TABLE XVIII.

| $n$. | $\alpha$. | | $\alpha/n$. | | $\alpha'/n' - \alpha/n$. | |
|---|---|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. | Found. | Calculated. |
| 1 | .. | ·0096 | .. | ·0096 | | |
| 2 | ·0214 | ·0212 | ·0107 | ·0106 | | ·0010 |
| 3 | ·0348 | ·0349 | ·0116 | ·0116 | ·0009 | ·0010 |
| 4 | ·0508 | ·0506 | ·0127 | ·0126 | ·0011 | ·0010 |
| 5 | ·0685 | ·0684 | ·0137 | ·0137 | ·0010 | ·0011 |
| 6 | ·0881 | ·0882 | ·0147 | ·0147 | ·0010 | ·0010 |

The relation between the amount of hydrogen iodide in a given volume of the liquid and the rate of change may also be exhibited graphically. The equation of the curve AB, Diagram 2, which is similar to equation (21), but shows more clearly the numerical relations, is $\alpha = n\,({\cdot}01 + {\cdot}001\,n)$. It expresses the rates of change with $n \times 6{\cdot}01\ HI$

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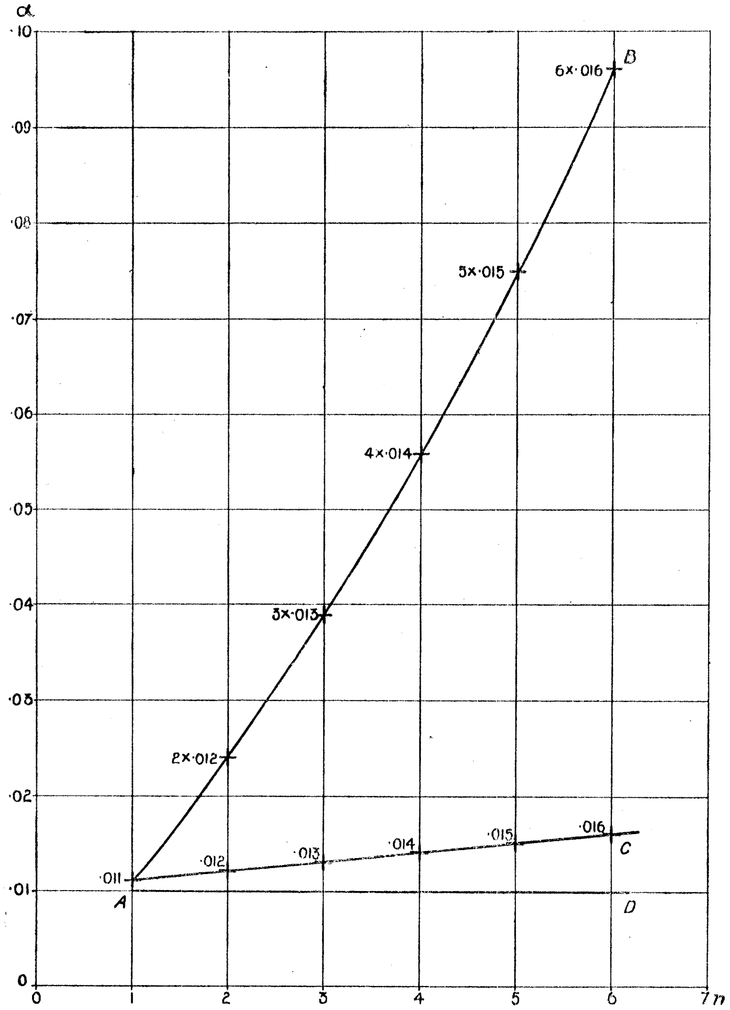
per cub. centim. at 34°.* The line A D is parallel to the base where $\alpha = {\cdot}01$ and represents what may be regarded in all cases as the initial rate, namely, the rate with one proportion of iodide ($6{\cdot}08\ i$) reacting with hydrogen dioxide, but not otherwise affecting the rate of change. But hydrogen iodide has a further influence upon the rate ; it adds to the initial rate a small fraction, which for one proportion of hydrogen

Diagram 2.



iodide in the case chosen is ·001, each additional proportion of hydrogen iodide adding the same amount. Thus, if hydrogen iodide could be added to the solution, as hydrogen sulphate and hydrogen chloride may, without increasing the amount of iodide present, the successive rates would be those represented by the line AC, of

---

* If in the quantity $(1180 + 19{\cdot}4\,i)$ of equation (22) $n$ is substituted for $i$, which $= \frac{1180}{194}$, or $6{\cdot}08\,i$, the quantity becomes $(1180 + 118\,n)$ ; and if the same substitution is made outside the bracket, equation (22) becomes $\alpha = n\,({\cdot}00718 + {\cdot}000718\,n)$. To raise the numbers within the bracket to $({\cdot}01 + {\cdot}001)$ the rate must be multiplied by 1·39, which would result from raising the temperature from 30° to 34°.

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which the equation is $\alpha = \cdot01 + \cdot001\,n$. But since the amount of iodide present is also increased, and the rate varies directly with the amount of iodide, the rates represented by AC must be multiplied by the number of proportions of hydrogen iodide taken, that is, by the values of $n$, giving the curve AB.

We may, perhaps, be allowed to illustrate the two-fold increase in the rate of change due to additions of hydrogen iodide by a simile. Some children are in a room playing at blind-man's buff. The child whose eyes are bandaged runs about among the others trying to catch one. It is a difficult task while the players are few; but as the number increases, the chance, or rate, of catching increases also. Not, however, directly with the number, as one might at first suppose, but in a greater degree. The joining in of more players has other incidental results. The blind-man is stimulated to greater efforts, and those who would escape impede one another. Thus each new-comer increases the chance of someone else being caught as well as adding the chance that he may be caught himself.

### *Variation of Sodium Hydrogen Carbonate.*

Of the many substances and classes of substances whose influence upon the change it might be interesting to try, we have only made systematic trial of one other, namely, sodium hydrogen carbonate. We chose this substance on two grounds: (1) it does not contain any element which is not already present in all the solutions with which we have worked, since water, carbonic acid, and sodium thiosulphate, are indispensable; (2) it seemed unlikely to undergo that double decomposition with sodium iodide which causes some uncertainty as to the substances actually present in the solution when a neutral iodide and hydrogen sulphate or chloride come together.

The amount of carbonic acid in the solutions was not determined; it may be considerably greater in presence of the sodium bicarbonate than in other solutions, and the relative effect of the acid may be greater; and these two causes may contribute to the unexpected result that the molecule $NaHCO^3$ accelerates the change more than $H^2SO^4$ or HCl.

On the other hand, the presence in the solution of such an amount of carbonic acid as dissolves in the slightly acid solutions we have generally used, is, in these solutions, without effect upon the rate. It was important to establish this point, especially in connexion with the inquiry into the effect of varying the temperature of the solution, since an increase of temperature also reduces the amount of carbonic acid dissolved. The following table gives the conditions and results of two sets of observations, one made in the ordinary manner, using large bubbles of carbonic acid to stir the liquid, the second being a repetition of the first, except that in place of carbonic acid, first nitrogen and then air were used. It will be seen that the intervals are very nearly the same in the two cases.

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### TABLE XIX.

203 $H^2SO^4$, 2·91 $KI$. Temperature, 17° C.

| Gas passed through the solution. | | |
|---|---|---|
| Carbonic acid. | Nitrogen. | Air. |
| Intervals.<br>Set I. | Intervals.<br>Set II. | |
| ′ | ′ | ′ |
| 3·43 | 3·37 | |
| 3·57 | 3·58 | |
| 3·72 | 3·65 | |
| 3·87 | 3·88 | |
| 4·05 | 3·95 | |
| 4·20 | 4·20 | |
| 4·40 | 4·40 | |
| 4·73 | 4·62 | |
| 4·87 | 4·87 | |
| 5·13 | 5·12 | |
| 5·45 | 5·38 | |
| 5·75 | 5·75 | |
| 6·17 | .. | 6·12 |
| 6·48 | .. | 6·50 |
| 7·03 | .. | 7·02 |

In Table XX. are given the conditions and results of twelve sets of observations in which the amount of sodium hydrogen carbonate present was varied.

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### Table XX.—25·2 $n$ $NaHCO^3$, 8·59 $NaI$. Temperature, 15° C.

$n = 1$, $y_0 = 7·32$.

| Intervals. | α. |
|---|---|
| 13′·73 | ·0107 |
| 16·12 | ·0107 |
| 19·67 | ·0106 |
| 24·93 | ·0105 |
| 33·80 | ·0106 |
| 52·35 | ·0108 |
| 133·75 | ·0106 |
| Mean rate . | ·0106 |

$n = 1$, $y_0 = 6·35$.

| Intervals. | α. |
|---|---|
| 16′·03 | ·0107 |
| 19·33 | ·0107 |
| 24·23 | ·0108 |
| 32·97 | ·0107 |
| 52·17 | ·0106 |
| 126·42 | ·0107 |
| Mean rate . | ·0107 |

$n = 2$, $y_0 = 6·2$.

| Intervals. | α. |
|---|---|
| 9′·87 | ·0184 |
| 11·40 | ·0187 |
| 14·65 | ·0185 |
| 20·42 | ·0183 |
| 32·75 | ·0185 |
| 97·25 | ·0184 |
| Mean rate . | ·0185 |

$n = 2$, $y_0 = 6·74$.

| Intervals. | α. |
|---|---|
| 8′·42 | ·0191 |
| 10·05 | ·0191 |
| 12·47 | ·0190 |
| (2) 40·27 | ·0190 |
| 44·70 | ·0191 |
| Mean rate . | ·0191 |

$n = 3$, $y_0 = 4·51$.

| Intervals. | α. |
|---|---|
| 9′·28 | ·0270 |
| 12·37 | ·0271 |
| 18·75 | ·0271 |
| 40·10 | ·0270 |
| Mean rate . | ·0271 |

$n = 4$, $y_0 = 5·14$.

| Intervals. | α. |
|---|---|
| 6′·10 | ·0355 |
| 7·78 | ·0355 |
| 10·82 | ·0355 |
| 17·82 | ·0354 |
| Mean rate . | ·0355 |

$n = 5$, $y_0 = 4·94$.

| Intervals. | α. |
|---|---|
| 5′·12 | ·0442 |
| 6·63 | ·0442 |
| 9·40 | ·0443 |
| 16·43 | ·0441 |
| Mean rate . | ·0442 |

$n = 6$, $y_0 = 4·45$.

| Intervals. | α. |
|---|---|
| 4′·65 | ·0547 |
| 6·28 | ·0546 |
| 9·73 | ·0540 |
| 21·45 | ·0546 |
| Mean rate . | ·0545 |

$n = 6$, $y_0 = 7·46$.

| Intervals. | α. |
|---|---|
| 2′·70 | ·0532 |
| 3·14 | ·0535 |
| 3·80 | ·0532 |
| 4·75 | ·0532 |
| 6·37 | ·0535 |
| 9·80 | ·0531 |
| 21·58 | ·0532 |
| Mean rate . | ·0533 |

$n = 7$, $y_0 = 7·5$.

| Intervals. | α. |
|---|---|
| 2′·28 | ·0627 |
| 2·69 | ·0621 |
| 3·24 | ·0619 |
| 4·07 | ·0619 |
| 5·40 | ·0624 |
| 8·28 | ·0618 |
| 17·80 | ·0621 |
| Mean rate . | ·0621 |

$n = 8$, $y_0 = 4·69$.

| Intervals. | α. |
|---|---|
| 3′·33 | ·0721 |
| 4·43 | ·0714 |
| 6·50 | ·0714 |
| 12·55 | ·0714 |
| Mean rate . | ·0716 |

$n = 9$, $y_0 = 7·41$.

| Intervals. | α. |
|---|---|
| 1′·83 | ·0793 |
| 2·15 | ·0789 |
| (2) 5·90 | ·0778 |
| 4·35 | ·0798 |
| 6·78 | ·0791 |
| 15·65 | ·0789 |
| Mean rate . | ·0790 |

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The rates thus found with from 25·2 $NaHCO^3$ per cub. centim. to nine times that quantity, form a series in arithmetical progression. They are compared in the following table with a series calculated from the equation

$$\alpha = {\cdot}00165 + {\cdot}00863\, n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23).$$

TABLE XXI.

| $n$. | $\alpha$. | | Differences $(\alpha' - \alpha)/(n' - n)$. | |
|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. |
| 1 | ·0106 | ·0103 | | |
| 2 | ·0188 | ·0189 | ·0082 | ·0086 |
| 3 | ·0271 | ·0275 | ·0083 | ·0086 |
| 4 | ·0355 | ·0362 | ·0084 | ·0087 |
| 5 | ·0442 | ·0448 | ·0087 | ·0086 |
| 6 | ·0539 | ·0534 | ·0097 | ·0086 |
| 7 | ·0621 | ·0621 | ·0082 | ·0087 |
| 8 | ·0716 | ·0707 | ·0095 | ·0086 |
| 9 | ·0790 | ·0793 | ·0074 | ·0086 |

If the number of $NaI$ and of $NaHCO^3$ per cub. centim. are represented by $i$ and $b$ the equation becomes

$$\alpha = i\,(192 + 40b) \times 10^{-6} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24).$$

## *Substitution of Atoms and Groups.*

Instead of varying the conditions of the change by taking more or less of some ingredients of the solution, it was possible to make a smaller variation, and thus, perhaps, to obtain more instructive results, by substituting salts with the same metal or acid radicle, one for another, in the proportion of their molecular masses. If, for instance, $n$ $NaI$ were substituted in each cub. centim. for $n$ $KI$, the actual substitution, of which the effect could be measured, would be that of so many sodium-atoms for the same number of potassium-atoms; and if $n$ $NaCl$ were similarly substituted for $n$ $NaHCO^3$, the actual exchange would be of chlorine-atoms for the same number of the monad radicles $HCO^3$. Although we are now inclined to think that what affects the character of a solution is the nature and number of the molecules, not of the atoms, in unit volume, and that therefore to make such a substitution is to make two changes at once, instead of the one change of only adding or only subtracting, we give the conditions and results of the experiments made from the above point of view.

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In the first set, the solutions of potassium iodide and of sodium iodide, of which equal quantities were taken, were found not to be equivalent; but by comparing one with another the two sets made with each iodide, the effects of each can be inferred, and thus the effect of substituting one for the other in molecular proportions.

### TABLE XXII.

57·2 $NaHCO^3$, $m$ (10·42 $KI$), $n$ (8·07 $NaI$). Temperature, 17° C.

| $m$. | $n$. | $\alpha$. | $\alpha/i$. |
|---|---|---|---|
| 1 | 0 | ·0273 | ·00262 |
| 0 | 1 | ·0216 | ·00267 |
| 3 | 0 | ·0850 | ·00272 |
| 0 | 3 | ·0669 | ·00276 |

Assuming the values of $\alpha$ from $m = 1$ to $m = 3$, and from $n = 1$ to $n = 3$, to increase, as in other cases, in arithmetical progression, the increment in the rate, with unit of iodide, per unit of $KI$ is $4·8 \times 10^{-6}$, and per unit of $NaI$ is $5·6 \times 10^{-6}$, at a temperature of 17°. Hence the effect of substituting $NaI$ for $KI$, or $Na$ for $K$, is to increase the rate, with unit of iodide, by the small quantity $·8 \times 10^{-6}$.

The next series was made by substituting for a part of the hydrogen chloride used in the initial set of observations, the corresponding molecular proportion of sodium chloride, a substitution which was readily effected by adding to successive solutions, made up with the same measure of hydrogen chloride, one, two, and three, smaller measures of a solution of sodium carbonate.

The conditions of these sets of observations, and the rates that were found, are given in the following Table, and are compared with a series of rates calculated from the formula,

$$\alpha = ·0384 - ·00534\, n,$$

which per unit of iodide and unit-substitution of $NaCl$ for $HCl$ becomes

$$\alpha = i\,(3690 - 6·14 \times 83·5\, n)\, 10^{-6}.$$

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### TABLE XXIII.

$(535 - 83{\cdot}5\,n)$ $HCl$, $83{\cdot}5\,n$ $NaCl$, $10{\cdot}42$ $KI$. Temperature, 16° C.

| $n$. | $\alpha$. | | $(\alpha - \alpha')/(n' - n)$. | |
|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. |
| 0 | ·0385 | ·0384 | ·0058 | ·0053 |
| 1 | ·0327 | ·0331 | ·0048 | ·0054 |
| 2 | ·0279 | ·0277 | ·0056 | ·0053 |
| 3 | ·0223 | ·0224 | | |

The effect of substituting in unit volume $NaCl$ for $HCl$, in presence of an unit of iodide at 16°, is, therefore, a decrement in the rate of $6{\cdot}14 \times 10^{-6}$. This may be compared with the effect of removing (instead of neutralizing) the same amount of hydrogen chloride, a number obtainable from equation (20) by applying the temperature-correction. The number thus found is $-6{\cdot}18 \times 10^{-6}$, showing that the influence of sodium chloride in a liquid containing hydrogen chloride is inappreciable. In the set of observations, in which the maximum quantity of sodium carbonate was taken, corresponding to a replacement of 250 out of 535 $HCl$ by 250 $NaCl$, the observed rate was ·0223. If 250 out of 535 $HCl$ had been omitted, and no sodium chloride added, the rate, so far as it can be inferred from observations made at 30°, would have been ·0223.

It appears, however, from the experiments which follow, that the influence upon the rate of sodium chloride, and doubtless, therefore, of other salts, is far greater in presence of sodium hydrogen carbonate than it is in presence of hydrogen chloride.

The substitution of which it was proposed to measure the influence, in a solution containing excess of sodium hydrogen carbonate, was that of chlorine for iodine, the proportions of sodium chloride and sodium iodide being so varied in successive experiments that the mass of sodium present in the liquid might be always the same. The conditions and results of these sets of observations are given in the following table. The effect of this substitution, according to the scheme given in the first two columns, is represented by the equation,

$$\alpha = n\,(26360 - 639n) \times 10^{-6} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25),$$

which per unit of iodide becomes

$$\alpha = i\,(5780 - 30{\cdot}7i) \times 10^{-6} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26).$$

From the coefficient of $i$ being negative, it appears that the rate of change is increased more by the presence of sodium chloride than by the presence (apart from

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its participation in the change) of sodium iodide. A substitution of iodide for chloride in molecular proportions causes in this respect a retardation; but, absolutely, each salt accelerates. To show their separate effect, equations (25) and (26) may be written

$$\alpha = n\,(22485 + 774m + 135n) \times 10^{-6} \text{ and } \alpha = i\,(4931 + 37{\cdot}2c + 6{\cdot}5i) \times 10^{-6}.$$

### TABLE XXIV.

92·6 $NaCO^3$, $m$ (4·56 $NaCl$), $n$ (4·56 $NaI$). Temperature 19°.

| $m$. | $n$. | $\alpha$. | | $\alpha/n$. | | $\alpha/n - \alpha'/n'$. | |
|---|---|---|---|---|---|---|---|
| | | Found. | Calculated. | Found. | Calculated. | Found. | Calculated. |
| 3 | 2 | ·0503 | ·0502 | ·0251 | ·0251 | | |
| 2 | 3 | ·0729 | ·0733 | ·0243 | ·0244 | ·0008 | ·0007 |
| 1 | 4 | ·0951 | ·0952 | ·0238 | ·0238 | ·0005 | ·0006 |
| 0 | 5 | ·1160 | ·1158 | ·0232 | ·0232 | ·0006 | ·0006 |

From equation (26) it appears that the effect of substituting, in unit volume and in presence of an unit of iodide, $NaCl$ for $NaI$, or $Cl$ for $I$, is to add, at a temperature of 19°, $30{\cdot}7 \times 10^{-6}$ to the rate. The effect of adding $NaI$ in presence of sodium hydrogen carbonate has been shown to be, at a temperature of 17°, an addition of $5{\cdot}6 \times 10^{-6}$, which would become, at a temperature of 19°, an addition of $6{\cdot}5 \times 10^{-6}$. From which it follows that the effect of adding $NaCl$ is $37{\cdot}2 \times 10^{-6}$. It is singular that the effect of $NaCl$ should be so much greater than that of $NaI$. Both salts have, in this case, a marked and measurable effect upon the rate, whereas, in presence of hydrogen chloride, the effect of the same small quantities of both is quite inappreciable.

The last comparison made from the substitution point of view was between $NaHCO^3$ and NaI, or $HCO^3$ and I. In this case, as the following table shows, the effect of the substitution of $NaI$ for $NaHCO^3$ is to diminish the rate with unit of iodide by ·00022/5·68 = 39 millionths.

### TABLE XXV.

(114·4 − 5·68$n$) $NaHCO^3$, 5·68$nNaI$. Temperature 19°.

| $n$. | $\alpha$. | $\alpha/i$. | $(\alpha/i - \alpha'/i')\,/\,(n' - n.)$ |
|---|---|---|---|
| 1 | ·0283 | ·00499 | |
| 3 | ·0774 | ·00455 | ·00022 |

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If the substitution here made is divided into an increase of sodium iodide and a diminution of sodium hydrogen carbonate, we can infer from these observations the effect upon the rate of the presence of $NaHCO^3$ at 19°. The increment due to an addition of $NaI$ at this temperature has been shown to be $6·5 \times 10^{-6}$, and hence the decrement due to a subtraction of $NaHCO^3$ is $39 + 6·5 = 45·5$ millionths.

### *Influence on the Rate of the Presence in the Solution of Various Substances.—Summary.*

In the tables which follow are put together the increments of the rate, with unit of iodide at the actual temperature, caused by the presence in each cubic centimetre of one millionth-gram molecule of each of the substances we have taken, such quantity of such substance being substituted for its own bulk of water. The three sets of numbers given under $H^2SO^4$ probably belong, as has been explained, to different hydrates of that substance. The numbers given are the number of millionths added to the rate—or fraction disappearing per minute—in consequence of the presence of each millionth-gram molecule per cubic centimetre. The degree of dilution which we thus adopt for comparison, may also be expressed by saying that each solution contains, per litre, a milligram-molecule of the substance, or that it is a millinormal solution.

Table XXVI.

| *t.* | $H^2SO^4$. | $H^2SO^4$. | $H^2SO^4$. | $HCl$. | $HI$. | $NaHCO^3$. |
|---|---|---|---|---|---|---|
| | 54 to 515. | 515 to 763. | 763 to 1143. | 71 to 355. | 7 to 44. | 25 to 227. |
| 15° | .. | .. | .. | .. | .. | 40 |
| 16 | 6·92 | 8·57 | 10·08 | | | |
| 20 | 9·10 | 11·27 | | | | |
| 30 | 18·00 | 22·50 | 26·50 | 16·8 | 19·4 | |

Table XXVII.—In presence of $NaHCO^3$.

| *t.* | $KI$. | $NaI$. | $NaCl$. |
|---|---|---|---|
| | 10 to 31. | 10 to 31. | 0 to 14. |
| 17° | 4·8 | 5·6 | |
| 19 | .. | .. | 37·2 |

In a solution containing hydrochloric acid the addition of sodium chloride, even in

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the relatively large quantity of 250 $NaCl$ per cubic centimetre did not affect the rate. We have only determined the influence of salts in presence of an excess of sodium hydrogen carbonate.

In the following table the increments given above have been reduced to their several values at 15°. The principles and method according to which this reduction has been made are explained in the section which follows on the variation of temperature.

TABLE XXVIII.—Temperature, 15°.

| $H^2SO^4$. | $H^2SO^4$. | $H^2SO^4$. | $HCl$. | $HI$. | $NaHCO^3$. |
|---|---|---|---|---|---|
| 54 to 515. | 515 to 763. | 763 to 1143. | 71 to 355. | 7 to 44. | 25 to 227. |
| 6·38 | 7·98 | 9·4 | 5·74 | 5·72 | 40 |

TABLE XXIX.—In presence of $NaHCO^3$. Temperature, 15°.

| $KI$. | $NaI$. | $NaCl$. |
|---|---|---|
| 10 to 31. | 10 to 31. | 0 to 14. |
| 4·15 | 4·84 | 27·7 |

## *Ionic Dissociation.*

During the interval between the publication of our former papers and the present time the hypothesis of the decomposition or dissociation* of compounds into their ions, by the act of solution, has met with general acceptance.

According to this hypothesis the dilute solutions of hydrogen chloride and potassium iodide, &c., which we have studied, contain a mixture of those substances with ions of hydrogen, chlorine, potassium, and iodine. The observation of the rate of change in solutions of different degrees of concentration might, perhaps, have furnished data regarding the extent of this ionic dissociation and its relation to

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* In terminology there is no appeal against usage; but whether nature recognizes any such distinction—corresponding apparently to that between divorce and judicial separation—as the term dissociation is used to express, may well be doubted. A substance which was one, and which under changed conditions becomes two or more, is not decomposed in a different way, nor do the newly-formed substances exist in a different state, according to the greater or less facility with which these substances can be brought under the conditions under which they will unite again.

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dilution. But our results do not seem to show any effect of progressive dilution beyond the necessary consequence that every addition of water diminishes proportionally the mass of each acid or salt in unit volume.

For example, the concentration of the potassium iodide in the experiments given in Table XV. was varied eightfold, from ·0146 normal to ·00182. Comparing unit-volumes of these two solutions, the more dilute solution contained, according to the hypothesis, less than one-eighth of the mass of potassium iodide in the stronger solution, since of that which remained a larger fraction was dissociated; and, correspondingly, the total mass of ions in unit volume of the more dilute solution was more than one-eighth of that present in the same volume of the stronger solution. If then the rate of interaction of ions is different from that of the molecules from which they are formed—if, for example, the time needed for the change, $nH^2O^2 + 2H'' + 2I'' = n(2H^2O + I^2)$, were different from that needed for $n(H^2O^2 + 2HI = 2H^2O + I^2)$—the total rate due to molecular and ionic interaction would vary with the amount of ionic dissociation. But it is not so; the rate with the more concentrated solution is ·108, the rate with the solution diluted eight-fold is ·0136, just one-eighth as great, the variation being simply proportional to the mass of substance acting. All our observations show the same fact, though some of the solutions were of more than normal (gram-molecule per litre) strength, and were diluted twenty- or thirty-fold, and others were varied from decinormal to much less than centinormal strength.

It seems to follow that the acids and salts which have been the subject of these experiments are either, (1) so near complete dissociation in solutions of normal strength that no great increase in the proportion of ions to molecules is caused by further dilution, or (2) that not much dissociation has yet taken place in solutions of less than centinormal strength, or (3) that the ions interact at the same rate, and accelerate chemical change in the same degree, as the molecules from which they are formed.

### *Reactions of Hydrogen Dioxide with Potassium Iodide and Iodine.*

Our previous paper concludes with the record of a number of sets of observations which showed that in a mixture of hydrogen iodide, with equal or with larger molecular proportions of potassium iodide, the rate of change is not proportional to the amount of hydrogen dioxide present at any moment.

We have shown that this result must occur whenever the rate observed is dependent upon more than one gradual change. If, for example, hydrogen dioxide converted potassium iodide into potassium iodate, and potassium iodate acted on hydrogen iodide or, in presence of carbonic acid and water, upon potassium iodide, then iodine would be formed both in this manner and directly by the interaction of hydrogen dioxide and hydrogen iodide. Now one at least of the changes $KI + 3H^2O^2 = 3H^2O + KIO^3$ and $KIO^3 + 6HI = KI + 3H^2O + 3I^2$ must happen gradually. Otherwise the whole

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of the hydrogen dioxide would be decomposed and the corresponding quantity of iodine formed at once. If the change $KI + 3H^2O^2 = 3H^2O + KIO^3$ happened at once, the rate of change might be normal, that is, proportional to the amount of iodate remaining at any moment, for potassium iodide being in excess all hydrogen peroxide would have disappeared; but if this change were gradual, then the rate of the observed change, that is, the formation of iodine, would be abnormal, unless the proportion of HI and KI molecules, and the rate of action of $H^2O^2$ upon each, were such that the rate of formation of iodine and of decomposition of hydrogen dioxide were the same by the single and by the double reaction. Such a coincidence could only happen in one of our sets of observations, in which the amount of potassium iodide was varied, and was very unlikely to happen at all. We have not further examined these subsidiary reactions, though it would be of interest to do so. Some other similar cases have been well investigated by Mr. PENDELBURY and Miss M. SEWARD ('Roy. Soc. Proc.,' vol. 45, p. 396).

In our mode of observing the rate of change we have brought into the solution a drop of sodium thiosulphate as quickly as possible after the appearance of the blue colour due to free iodine. Our object in doing so has been to keep constant the amount of iodide with which the hydrogen dioxide was reacting; but the practice proved to be also necessary, in certain cases at least, for another reason, namely, that iodine may act upon sodium or hydrogen dioxide. Such an action, irregularly diminishing from time to time the amount of the substance whose rate of disappearance was being measured, would throw our results into confusion. As a rule it has not occurred, and we believe such a change does not happen at all in very dilute acid solutions of iodine. But in presence of sodium hydrogen carbonate it may happen; and in view of the result we are about to describe we think it likely that some of the discrepancies which may be noticed in the observations and rates given on Tables XX. and XXI. may be due to this cause.

With the view of reducing to a minimum, in comparing the effect upon the rate of different quantities of sodium iodide, that part of the acceleration which is due to the increase of the saline ingredients of the liquid, a solution was prepared containing per cub. centim. 686 $NaHCO^3$ and ·211 $NaI$. To this the usual measure of dioxide was added, and after a considerable lapse of time, the liquid being fully charged with carbonic acid, no change of colour had occurred. A second proportion of iodide was added; still no iodine was liberated. Some solution of iodine was dropped into the liquid; on stirring, the blue colour at once disappeared. Instead of liberating, the dioxide was now fixing iodine. Or rather, both actions were going on simultaneously, but with such unequal velocities that the iodine formed was kept down, as when sodium thiosulphate is present, to an infinitesimal quantity, insufficient to impart a perceptible blue tinge to the solution of starch. On repeating the experiment with rather less of the bicarbonate and more iodide we found that the addition of dioxide produced a pale blue colour which did not deepen. When a drop of a dilute solution of sodium

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thiosulphate was added, the colour became fainter or disappeared, but soon returned. When a drop of dilute chlorine water was added, the colour deepened, but soon faded to its original paleness. This stability of colour the liquid retained as long as the dioxide lasted.

The explanation of this rather striking phenomenon seems to be as follows. The formation of iodine by the interaction of dioxide and iodide takes place as in other cases, $2NaI + H^2O^2 + 2CO^2 = NaHCO^3 + I^2$; but the removal of iodine, probably according to the equation $2NaHCO^3 + H^2O^2 + I^2 = 2NaI + 2H^2O + 2CO^2 + 0^2$, takes place also. The number of occurrences of these changes in unit time is directly proportional in both cases to the amount of dioxide present, and also, in the first case, to the amount of iodide, in the second, to the amount of iodine. The rate of each change is also influenced by the amount of sodium hydrogen carbonate present, and the temperature of the solution. When first sodium dioxide is added to the solution, and there at once converted into hydrogen dioxide and sodium hydrogen carbonate,—$Na^2O^2 + 2H^2O + 2CO^2 = H^2O^2 + 2NaHCO^3$,—the dioxide reacts with the iodide, and iodine is formed. The amount of iodine increases, at first more quickly, then more and more slowly, until—the rate of its reconversion into iodide increasing proportionally with its increase—it is being removed as fast as it is formed. Thenceforward the amount of iodine in the liquid, and therefore the depth of the blue colour, is constant; the two changes exactly balance and undo one another. The only permanent result is the decomposition of the dioxide, which proceeds just twice as fast (except for a minute diminution in the amount of iodide present) as it would if the appearance, and practically the formation, of iodine were prevented by an addition of thiosulphate. As the dioxide diminishes, iodine is formed more slowly, and is reduced more slowly, always in the same proportion. When the balance is upset by an addition of thiosulphate or of chlorine water, iodine is formed more quickly than it is reduced, or reduced more quickly than it is formed, until its amount, and the colour of the liquid, is the same as before.

## *Variation of Temperature.*

Tables XXX. to LIV. contain the results of experiments upon the effect of varying the temperature of the solution, in which the change takes place, and of calculations relating to them. In all the sets of experiments, except those recorded in Table XXXVIII., the volume of the solution was measured at the same temperature, and not at the temperature at which the experiment was made, so that a cub. centim. contained at different temperatures different quantities of the substances which affect the rate of change. But the rates at different temperatures cannot be compared unless the change has taken place with the same amounts of substances in each unit of volume. A correction has, therefore, to be applied to the rates actually found, to reduce them to the rates which would have been obtained if the solution had been brought at each

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temperature to the same volume after the introduction of the various substances. This correction can be applied from existing data for all the substances except water. The experiments recorded in Table XXXVIII. were made in solutions brought at each temperature to the same volume, containing thus in each cub. centim. a constant amount of hydrogen sulphate and iodide, but a continually diminishing quantity of water as the temperature was increased. It will be seen hereafter that the effect of this diminution, if any, is so small as not to affect the rate by an amount exceeding the limits of possible experimental error.

From the series of rates in Tables XXX., XXXVI., &c., a new series of rates was obtained, for which the quantities of substances in each unit volume of the solution at any temperature were taken to be the same as at zero. This new series was calculated in the following way.

Let the volume of the solution which is $V_0$ at zero be $V_0(1+\mu)$ at $t^\circ$, and the number of units of the substances introduced into the solution be, of iodide I, of other substances not undergoing change (including water), $X_1$, $X_2 \ldots$, and let $a$ be the rate at $t^\circ$ with unit of iodide, $b$ the increment of this rate per unit of iodide, $b_1$, $b_2 \ldots$ the increment of this rate per unit of each of the other substances; then the rate $\alpha$ actually found is equal to

$$\frac{\mathrm{I}}{V_0(1+\mu)}\left\{a + b\frac{\mathrm{I}}{V_0(1+\mu)} + b_1\frac{X_1}{V_0(1+\mu)} + b_2\frac{X_2}{V_0(1+\mu)} + \ldots\right\} \quad . \quad . \quad (27),$$

and the rate $\alpha'$ which would have been found with the same amounts of substances per unit volume as there were in the solution at a temperature zero is

$$\frac{\mathrm{I}}{V_0}\left\{a + b\frac{\mathrm{I}}{V_0} + b_1\frac{X_1}{V_0} + b_2\frac{X_2}{V_0} + \ldots\right\} \quad . \quad . \quad . \quad . \quad (28),$$

from (27),

$$\alpha(1+\mu)^2 = \frac{\mathrm{I}}{V_0}\left\{a(1+\mu) + b\frac{\mathrm{I}}{V_0} + b_1\frac{X_1}{V_0} + \ldots\right\} = \alpha' + \frac{a\mu\mathrm{I}}{V_0},$$

or,

$$\alpha' = \alpha(1+\mu)^2 - a\mu i, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29),$$

$i$ being the amount of iodide in unit volume of the solution when its temperature is zero. The quantity $\mu$ was determined by a series of observations of the expansion in solutions of the same composition as those used in the experiments; the quantity $a$ is known for 30° from the equation (22), p. 842, and for other temperatures by interpolation from the series of experimental rates, the term $a\mu i$ in which it occurs being so small that the approximation is sufficiently exact.

The following table contains the results of a set of experiments at different temperatures in solutions containing 203 $H^2SO^4$ and 7·28 $HI$. The values of $t$ are the corrected temperatures corresponding to the actual readings of our thermometer at 0°, 5°, 10°, &c.

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## Table XXX.

$(203 - 7\cdot28z)\ H^2SO^4,\ 7\cdot28\ \{(1 - z)\ KI + zHI\},\ 7\cdot28zKHSO^4$. Temperature, $t°$ C.

| $t = 0$, $y_0 = 17\cdot3$. | |
|---|---|
| Intervals. | α |
| ′ 14·27 | ·00418 |
| 14·77 | ·00429 |
| (2) 31·38 | ·00446 |
| 17·87 | ·00438 |
| 19·62 | ·00433 |
| 21·45 | ·00433 |
| 23·65 | ·00432 |
| 26·37 | ·00432 |
| Mean rate | ·00433 |

| $t = 4\cdot96$, $y_0 = 17\cdot2$. | |
|---|---|
| Intervals. | α. |
| ′ 9·70 | ·00617 |
| 10·33 | ·00617 |
| 10·95 | ·00622 |
| 11·78 | ·00620 |
| 12·63 | ·00621 |
| 13·70 | ·00622 |
| 15·03 | |
| Mean rate | ·00620 |

| $t = 10\cdot11$, $y_0 = 17\cdot25$. | |
|---|---|
| Intervals. | α. |
| ′ 6·63 | ·00900 |
| 7·08 | ·00898 |
| 7·52 | ·00902 |
| Mean rate | ·00900 |

| $t = 15\cdot08$, $y_0 = 13\cdot25$. | |
|---|---|
| Intervals. | α. |
| ′ 6·1 | ·0129 |
| 6·6 | ·0129 |
| 7·23 | ·0129 |
| Mean rate | ·0129 |

| $t = 15\cdot08$, $y_0 = 9\cdot2$. | |
|---|---|
| Intervals. | α. |
| ′ 8·97 | ·0128 |
| 10·10 | ·0129 |
| 11·52 | ·0130 |
| 13·72 | ·0128 |
| 16·92 | ·0126 |
| 21·03 | ·0129 |
| Mean rate | ·0128 |

| $t = 20\cdot03$, $y_0 = 9\cdot04$. | |
|---|---|
| Intervals. | α. |
| ′ 7·17 | ·0185 |
| 8·30 | ·0185 |
| 9·73 | ·0186 |
| 12·02 | ·0184 |
| 15·37 | ·0185 |
| 21·43 | ·0186 |
| 35·73 | ·0188 |
| Mean rate . | ·0186 |

| $t = 20\cdot34$, $y_0 = 9\cdot25$. | |
|---|---|
| Intervals. | α. |
| ′ 6·17 | ·0185 |
| 6·87 | ·0188 |
| 7·92 | ·0187 |
| Mean rate . | ·0187 |

| $t = 25\cdot09$, $y_0 = 5\cdot25$. | |
|---|---|
| Intervals. | α. |
| ′ 8·23 | ·0257 |
| 10·43 | ·0257 |
| 14·30 | ·0257 |
| 22·82 | ·0258 |
| Mean rate . | ·0257 |

| $t = 30\cdot05$, $y_0 = 5\cdot23$. | |
|---|---|
| Intervals. | α. |
| ′ 5·83 | ·0363 |
| 7·57 | ·0357 |
| 10·33 | ·0359 |
| 16·57 | ·0359 |
| 46·68 | ·0359 |
| Mean rate . | ·0359 |

| $t = 35\cdot05$, $y_0 = 6\cdot23$. | |
|---|---|
| Intervals. | α. |
| ′ 3·57 | ·0490 |
| 4·27 | ·0497 |
| 5·37 | ·0503 |
| 7·38 | ·0503 |
| 12·30 | ·0483 |
| 33·75 | ·0497 |
| Mean rate . | ·0495 |

| $t = 40\cdot05$, $y_0 = 7\cdot72$. | |
|---|---|
| Intervals. | α. |
| ′ 2·03 | ·0684 |
| 2·32 | ·0695 |
| 2·80 | ·0686 |
| 3·43 | ·0695 |
| 4·54 | ·0689 |
| 6·66 | ·0689 |
| 12·59 | ·0691 |
| Mean rate . | ·0690 |

| $t = 45\cdot01$, $y_0 = 8\cdot09$. | |
|---|---|
| Intervals. | α. |
| ′ 1·38 | ·0955 |
| 1·60 | ·0951 |
| 1·87 | ·0957 |
| 2·33 | ·0940 |
| 2·95 | ·0948 |
| 4·13 | ·0946 |
| 6·85 | ·0951 |
| 25·23 | ·0953 |
| Mean rate . | ·0950 |

| $t = 50\cdot18$, $y_0 = 8$. | |
|---|---|
| Intervals. | α. |
| ′ 1·00 | ·133 |
| 1·18 | ·131 |
| 1·37 | ·133 |
| 1·70 | ·131 |
| 2·20 | ·131 |
| 3·08 | ·131 |
| 5·33 | ·130 |
| Mean rate . | ·131 |

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The following table gives the series of rates, corrected by the equation (29), p. 856, corresponding to those in the preceding table. The ingredients in a cubic centimetre of the solution were at zero,

$$(203{\cdot}3 - 7{\cdot}29z)\ H^2SO^4, \quad 7{\cdot}29\{(1 - z)\ KI + zHI\}, \quad 7{\cdot}29zKHSO^4,$$

and the values of $\alpha$ are calculated from those in Table XXX so as to represent the rates which would have been found if the solution had been made up at the temperature of each set of observations, so as to contain these amounts per cubic centimetre.

TABLE XXXI.

| $t$. | $\alpha$. |
|---|---|
| 0·00 | ·00433 |
| 4·96 | ·00621 |
| 10·11 | ·00902 |
| 15·08 | ·01294 |
| 20·34 | ·01871 |
| 25·09 | ·02590 |
| 30·05 | ·03630 |
| 35·05 | ·05010 |
| 40·05 | ·07010 |
| 45·01 | ·09700 |
| 50·18 | ·13400 |

To facilitate the investigation of the law of connexion between $\alpha$ and $t$, a calculation was made, by interpolation, of the rates at degrees of temperature expressed in whole numbers. The following table gives these rates, their logarithms to the base 10, and the successive differences of the logarithms.

TABLE XXXII.

| $t$. | $\alpha$. | Log $\alpha$. | $\Delta$ log $\alpha$. |
|---|---|---|---|
| 0 | ·00433 | $\bar{3}{\cdot}636$ | |
| 5 | ·00622 | $\bar{3}{\cdot}794$ | ·158 |
| 10 | ·00896 | $\bar{3}{\cdot}952$ | ·158 |
| 15 | ·01282 | $\bar{2}{\cdot}108$ | ·156 |
| 20 | ·01832 | $\bar{2}{\cdot}263$ | ·155 |
| 25 | ·02570 | $\bar{2}{\cdot}410$ | ·147 |
| 30 | ·03620 | $\bar{2}{\cdot}559$ | ·149 |
| 35 | ·05000 | $\bar{2}{\cdot}699$ | ·140 |
| 40 | ·07000 | $\bar{2}{\cdot}845$ | ·146 |
| 45 | ·09700 | $\bar{2}{\cdot}987$ | ·142 |
| 50 | ·13270 | $\bar{1}{\cdot}123$ | ·136 |

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It was at first thought that $\Delta \log \alpha$ was constant, and the values of this expression over the range of temperature from zero to 20° are not far from constant; but an examination of the values from zero to 50° shows that they continually diminish as the temperature increases. As a first approximation to the law of connexion between $\alpha$ and $t$ the values of $\Delta \log \alpha$ may be assumed to be in arithmetical progression; so that we may put $\Delta \log \alpha_x = a - bx$. The most probable values of $a$ and $b$ are ·16005 and ·0025, which give for the series $\Delta \log \alpha$, ·16005, ·15755, ·15505, ·15255, ·15005, ·14755, ·14505, ·14255, ·14005, ·13755, and for the corresponding series of values of $\log \alpha$ $\bar{3}$·635, $\bar{3}$·795, $\bar{3}$·953, $\bar{2}$·108, $\bar{2}$·260, $\bar{2}$·410, $\bar{2}$·558, $\bar{2}$·703, $\bar{2}$·845, $\bar{2}$·985, $\bar{1}$·123. These values are fairly concordant with the experimental values, and the formula

$$\log \alpha = \bar{3}{\cdot}6354 + {\cdot}1613x - {\cdot}00125x^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

would give the rates at intermediate temperatures with sufficient accuracy, $5x$ being the number of degrees counted from zero, C. This formula, however, would evidently fail for higher degrees of temperature, for the difference between successive values of $\log \alpha$ would vanish when $x = {\cdot}16005 \div {\cdot}0025$, or at a temperature of 320°, and the rate would be equal to the rate at zero when $x = {\cdot}1613 \div {\cdot}00125$, or at a temperature of 645°. The rates on this hypothesis would first increase and then diminish, so that the formula can only be regarded as convenient for calculating the rates at different temperatures ranging from zero to 50°.

A function of $x$, the successive differences of which closely resemble the successive differences of $\log \alpha$, is $u_x = \log (c + x)$, when $c$ is considerably larger than $x$; the second differences of this function slowly diminish as $x$ increases, and if a series of approximate values of this function were given for values of $x$ ranging from zero to 10°, it might easily be supposed that the successive differences formed an arithmetical progression, and if the assumption $\Delta u_x = a - bx$ were made and the most probable values of $a$ and $b$ found, the values of $u_x$ calculated on this hypothesis would not differ sensibly from the actual values.

Assuming, then, that

$$\log \alpha_x = m \log \left(\frac{c + x}{c}\right) + \log \alpha_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31),$$

the problem is to determine the values of $m$ and $c$ from the experimental numbers. First, for these substitute the more orderly series of numbers calculated from the formula $\Delta \log \alpha_x = a - bx$, then suppose that these agree with the series of numbers calculated in a similar way from $m\Delta \log (c + x) = a - bx$; it is clear that the three series $\Delta \log \alpha_x$, $m\Delta \log (c + x)$, $a - bx$ will agree with a high degree of approximation for a value of $x$ equidistant from its first and last values.

Taking this value of $x$ to be 5, the assumption gives, from the values printed above,

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$$m\Delta \log (c + 5) = \cdot 15005 \quad . \quad . \quad . \quad (32),$$

$$m\Delta \log (c + 6) = \cdot 14755 \quad . \quad . \quad . \quad (33).$$

Now

$$\Delta \log (c + 6) = \log \frac{c + 7}{c + 6}$$

$$= \log \left(1 + \frac{1}{c + 6}\right) = \log \left\{1 + \frac{1}{(c + 5)\left(1 + \frac{1}{c + 5}\right)}\right\}$$

$$= \log \left\{1 + \frac{1}{c + 5}\left(1 - \frac{1}{c + 5} + \frac{1}{(c + 5)^2} - \ldots\right)\right\}$$

$$= \log \left[\frac{c + 6}{c + 5}\left\{1 - \frac{1}{(c + 5)(c + 6)} + \ldots\right\}\right]$$

$$= \log \frac{c + 6}{c + 5} - \frac{\log e}{(c + 5)(c + 6)} \text{ approximately}$$

$$= \Delta \log (c + 5) - \frac{\log e}{(c + 5)(c + 6)} \quad . \quad . \quad . \quad (34),$$

so that

$$\frac{m \log e}{(c + 5)(c + 6)} = \cdot 0025 \quad . \quad . \quad . \quad (35),$$

and (32),

$$m \Delta \log (c + 5) = \cdot 15005 \quad . \quad . \quad . \quad (36).$$

Therefore

$$(c + 5)(c + 6) \log \frac{c + 6}{c + 5} = 60 \cdot 02 \log e = 26 \cdot 066 \quad . \quad . \quad . \quad (37).$$

This equation is approximately satisfied by $c = 54 \cdot 52$, which gives for the value of the expression on the left hand, 26·065.

It is probable then that the series of values of $\log \alpha$ is satisfied by an equation of the form

$$\log \alpha_x = m \log \frac{c + x}{c} + \log \alpha_0 \quad . \quad . \quad . \quad (38),$$

$c$ having the value 54·52; but since $5x = t$, this is the same as

$$\log \alpha_t = m \log \frac{272 \cdot 6 + t}{272 \cdot 6} + \log \alpha_0 \quad . \quad . \quad . \quad (39),$$

or,

$$\frac{\alpha_t}{\alpha_0} = \left(\frac{272 \cdot 6 + t}{272 \cdot 6}\right)^m \quad . \quad . \quad . \quad (40).$$

This equation implies that no chemical change will take place when $t = - 272 \cdot 6$,

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a temperature at once recognised as almost identical with that usually assumed as the temperature of the absolute zero, viz., $-273°$ C. At this point molecules are at rest, and hence gases have no tension and chemical change ceases. Thus, within the limits of experimental errors, it may be assumed that the zero of chemical change coincides with the zero of absolute temperature. If we call the absolute temperature at the freezing point $T_0$, the equation of connexion of the amount of chemical change with temperature may be written in the form

$$\frac{\alpha_T}{\alpha_{T_0}} = \left(\frac{T}{T_0}\right)^m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41),$$

T being the absolute temperature corresponding to $t$ degrees on the ordinary scale. In the subsequent discussion of experimental results $T_0$ expresses the absolute temperature 273° C. The form of the equation shows that the relation between the amount of chemical change at a given temperature and the absolute temperature is independent of the units in which each of these quantities is measured. It will be seen subsequently that the number $m$, which remains constant in a series of experiments at different temperatures with the same kind of solution, varies with the nature of the main ingredient of the solution but not with the amount of that ingredient.

The differential equation corresponding to the integral equation is

$$\frac{d\alpha}{\alpha} \Big/ \frac{dT}{T} = m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42),$$

so that if $\alpha$, $\alpha'$ are two rates corresponding to two temperatures very near to each other,

$$\frac{\alpha' - \alpha}{\alpha} \Big/ \frac{T' - T}{T} = m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (43);$$

this relation implies that the increment of each unit of chemical change, due to a small rise of temperature, is proportional to the increment of each unit of temperature; or the increase of each unit of chemical change per unit increment of each unit of temperature is constant at all temperatures.

These statements are illustrated graphically on Diagram 3, p. 862, by the curve APP′. The value of $m$ in the formula $\alpha/\alpha_0 = (T/T_0)^m$, which has been calculated from the experimental numbers in a manner explained subsequently, is 20·38. The curve APP′ represents the above formula with this value of $m$. The rate at zero C. is taken as the unit rate. The rate at any temperature $t°$ C., or $273° + t°$, counting from the absolute zero, is calculated from the formula

$$\alpha = (T/T_0)^{20 \cdot 38}, \text{ or } \{(273+t)/273\}^{20 \cdot 38} \quad . \quad . \quad . \quad . \quad . \quad . \quad (44).$$

The following table gives the values of $\alpha$ corresponding to the values of $t$:

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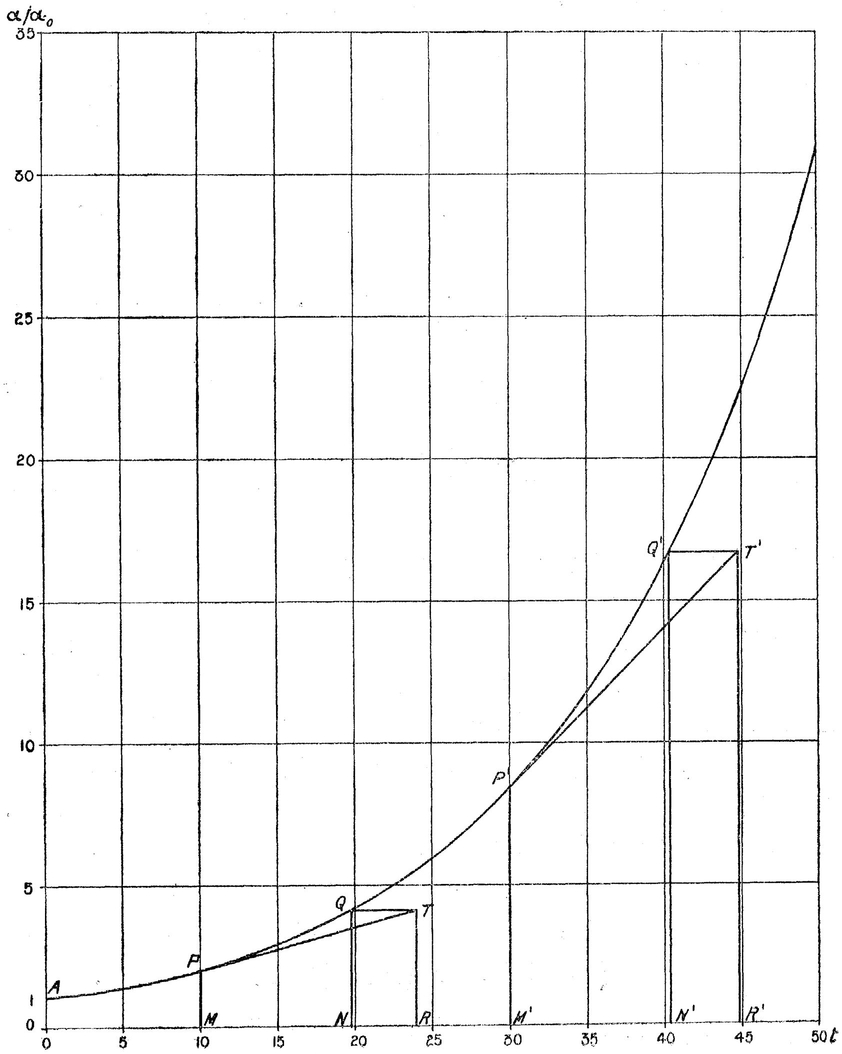
TABLE XXXIII.

| $t$. | $a$. |
|---|---|
| 0 | 1·00 |
| 5 | 1·44 |
| 10 | 2·08 |
| 15 | 2·97 |
| 20 | 4·23 |
| 25 | 5·96 |
| 30 | 8·38 |
| 35 | 11·67 |
| 40 | 16·22 |
| 45 | 22·39 |
| 50 | 30·77 |

Diagram 3.



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The amount of chemical change at zero being 1·00, the amount at 10° is 2·08, represented by MP, *i.e.*, the rate is rather more than doubled by a rise of temperature of 10° from zero to 10°; if the increase of chemical change per unit of temperature were supposed to remain constant at this point P, *i.e.*, if the relation between chemical change and temperature were represented by the tangent PT at P instead of the curve PP′, the amount of change would be doubled when the temperature had been increased by $T/m = 283/20·38$ or 13·9° C., represented by MR. The actual increase of temperature MN, which doubles the rate at P, is obtained by drawing TQ parallel to MR, to meet the curve in Q, and QN parallel to PM, to meet MR in N. It is seen that MN is rather less than 10°, the amount of change at 20° being 4·23 units. A similar construction is made for the change at 30°, represented by $M'P' = 8·38$ units; P′T′ is the tangent at P′, $R'T' = 2M'P'$, $M'R' = 14·9°$; the change being actually doubled by an increase of temperature, represented by M′N′, of a little more than 10°, the change at 40° being 16·22 units. Also the ratio MR : M′R′ is equal to the ratio of the absolute temperatures at P and P′, viz., 13·9 : 14·9=283 : 303, and the increments of each unit of change per degree centigrade at P and P′, measured by $\frac{RT - MP}{MR \, . \, MP}$ or $\frac{1}{MR}$ and by $\frac{R'T' - M'P'}{M'R' \, . \, M'P'}$ or $\frac{1}{M'R'}$, are inversely as the absolute temperatures at P and P′, viz., are in the ratio 303 : 283; in other words, the increase of unit change per degree centigrade is $\frac{1}{MR}$, or ·072, at 10°, and $\frac{1}{M'R'}$, or ·067, at 30°.

It is also convenient to express the relation between chemical change and temperature in the form in which it originally presented itself, viz.,

$$\log \alpha - \log \alpha_0 = m (\log T - \log T_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45),$$

and to state this relation concisely by saying that the logarithmic increment of chemical change due to increase of temperature varies as the logarithmic increment of absolute temperature. This mode of stating the law has the advantage that the graphic representation of the relation is a straight line, as is shown in Diagram 4, p. 864. The divisions of the horizontal axis in this mode of representation are the logarithms of $T/T_0$, and the divisions of the vertical axis are the logarithms of $\alpha/\alpha_0$. Fig. 1, Diagram 4, represents in this manner the same relation as that represented by the curve in Diagram 3. The numbers are calculated from the formula

$$\log (\alpha/\alpha_0) = 20·38 \log (T/T_0), \text{ or } 20·38 \log \{(273 + t)/273\} \quad . \quad . \quad (46),$$

and are given in the following table :—

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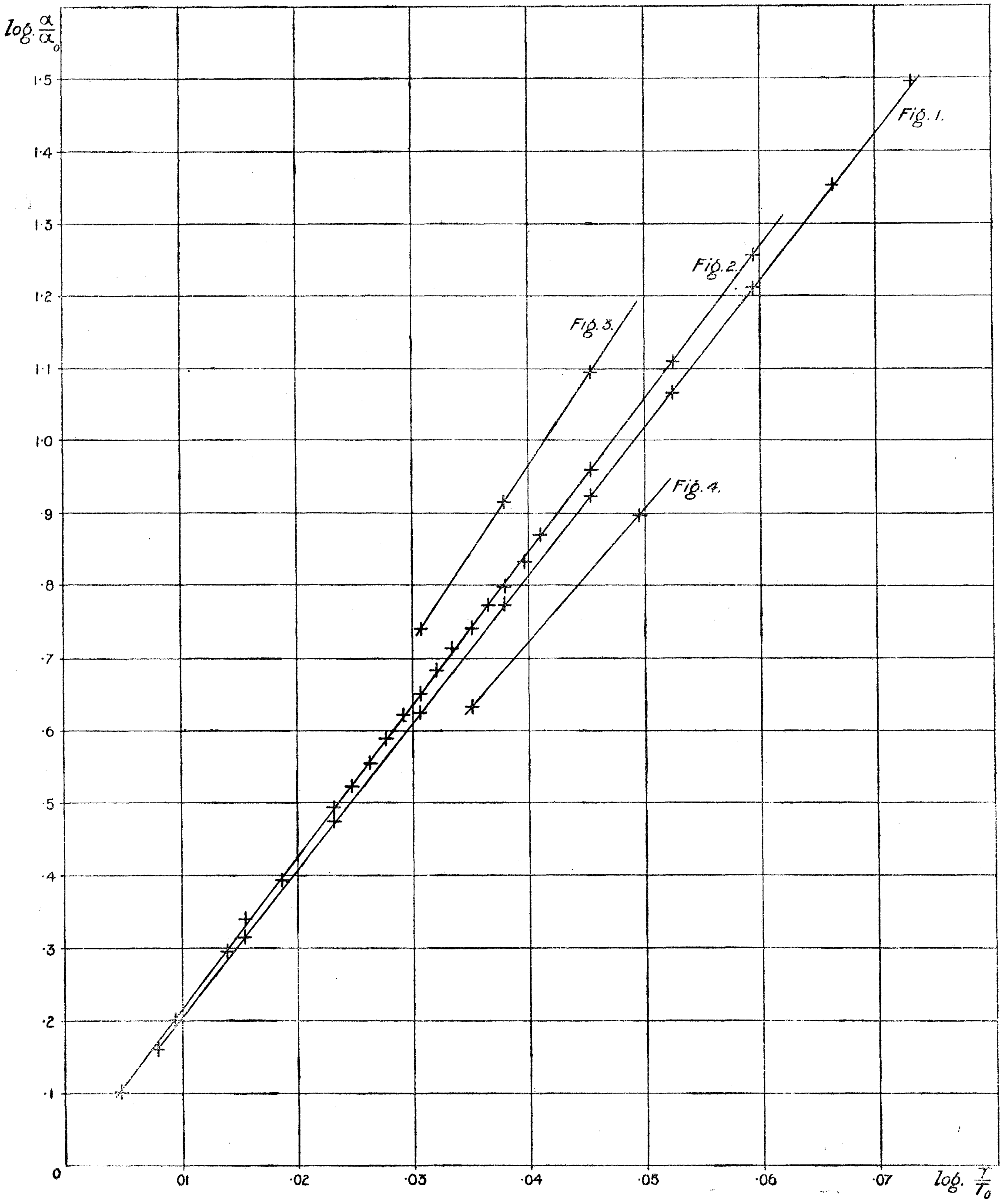
Diagram 4.



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### TABLE XXXIV.

| $t$. | Log $(T/T_0)$. | Log $(\alpha/\alpha_0)$. |
|---|---|---|
| 0 | ·0000 | 0·000 |
| 5 | ·0079 | 0·160 |
| 10 | ·0156 | 0·318 |
| 15 | ·0232 | 0·473 |
| 20 | ·0307 | 0·626 |
| 25 | ·0380 | 0·775 |
| 30 | ·0453 | 0·923 |
| 35 | ·0524 | 1·067 |
| 40 | ·0594 | 1·210 |
| 45 | ·0663 | 1·350 |
| 50 | ·0730 | 1·488 |

Assuming, then, as a highly probable expression of the law of connexion between the chemical change which we have studied and temperature, at least for the range from zero to 50°, the equation

$$\log(\alpha/\alpha_0) = m \log(T/T_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47),$$

a determination was made of the most probable values of $m$ and $\log \alpha_0$ for the series of numbers in Table XXXI. These were found to be $m = 20\cdot38$, $\log \alpha_0 = \bar{3}\cdot635$. The values of $\log \alpha$ and $\alpha$ given by these are compared in the following table with the values found by experiment.

### TABLE XXXV.

$(203\cdot3 - 7\cdot29z)\,H^2SO^4$, $7\cdot29\,\{(1-z)\,KI + zHI\}$, $7\cdot29\,zKHSO^4$.

| $t$. | $\log \alpha$. | | $\alpha$. | |
|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. |
| 0 | $\bar{3}\cdot636$ | $\bar{3}\cdot635$ | ·00433 | ·00432 |
| 5 | $\bar{3}\cdot794$ | $\bar{3}\cdot796$ | ·00622 | ·00625 |
| 10 | $\bar{3}\cdot952$ | $\bar{3}\cdot953$ | ·00896 | ·00898 |
| 15 | $\bar{2}\cdot108$ | $\bar{2}\cdot108$ | ·01282 | ·01284 |
| 20 | $\bar{2}\cdot263$ | $\bar{2}\cdot261$ | ·01830 | ·01820 |
| 25 | $\bar{2}\cdot410$ | $\bar{2}\cdot410$ | ·02570 | ·02570 |
| 30 | $\bar{2}\cdot559$ | $\bar{2}\cdot558$ | ·03620 | ·03610 |
| 35 | $\bar{2}\cdot699$ | $\bar{2}\cdot703$ | ·05000 | ·05040 |
| 40 | $\bar{2}\cdot845$ | $\bar{2}\cdot845$ | ·07000 | ·07000 |
| 45 | $\bar{2}\cdot987$ | $\bar{2}\cdot985$ | ·09700 | ·09670 |
| 50 | $\bar{1}\cdot123$ | $\bar{1}\cdot123$ | ·13300 | ·13300 |

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The calculated values of $\alpha$ agree within the limits of experimental error with the values determined by experiment. For the range of temperature from zero to 50° the law is established, and the assumption that the zero of the particular chemical change here considered coincides with the absolute zero of temperature is justified.

To confirm this result another set of experiments was made with the same amount of hydrogen sulphate and half the amount of potassium iodide, the results of which are recorded in the following table.

### TABLE XXXVI.

$(203 - 3{\cdot}64z)\,H^2SO^4$, $3{\cdot}64\,\{(1 - z)\,KI + zHI\}$, $3{\cdot}64zKHSO^4$. Temperature $t$° C.

| $t = 20{\cdot}34$, $y_0 = 17$. | | $t = 30{\cdot}05$, $y_0 = 13$. | | $t = 40{\cdot}05$, $y_0 = 8$. | | $t = 50{\cdot}18$, $y_0 = 4$. | |
|---|---|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 6′·48 | ·00933 | 4′·43 | ·0181 | 3′·83 | ·0348 | 4′·25 | ·0678 |
| 7·00 | ·00923 | 4·85 | ·0179 | 4·43 | ·0348 | 6·07 | ·0669 |
| 7·50 | ·00918 | 5·23 | ·0182 | 5·22 | ·0349 | | |
| Mean rate . | ·00925 | Mean rate . | ·0181 | Mean rate . | ·0348 | Mean rate . | ·0673 |

The values of $\alpha$ in this table were corrected for expansion as in the previous case, and values corresponding to whole numbers of degrees of temperature obtained by interpolation. The most probable value of $m$ is, as before, 20·38, and of log $\alpha_0$, $\bar{3}{\cdot}335$.

The following table exhibits the agreement of the experimental and calculated numbers.

### TABLE XXXVII.

$(203{\cdot}3 - 3{\cdot}645z)\,H^2SO^4$, $3{\cdot}645\,\{(1 - z)\,KI + zHI\}$, $3{\cdot}645zKHSO^4$.
Temperature $t$° C.

| $t$. | Log $\alpha$. | | $\alpha$. | |
|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. |
| 0 | | $\bar{3}{\cdot}335$ | | ·0022 |
| 20 | $\bar{3}{\cdot}957$ | $\bar{3}{\cdot}961$ | ·0091 | ·0091 |
| 30 | $\bar{2}{\cdot}261$ | $\bar{2}{\cdot}258$ | ·0182 | ·0181 |
| 40 | $\bar{2}{\cdot}547$ | $\bar{2}{\cdot}550$ | ·0352 | ·0355 |
| 50 | $\bar{2}{\cdot}833$ | $\bar{2}{\cdot}829$ | ·0681 | ·0675 |

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A third set of experiments was made with $468 H^2SO^4$ and $4{\cdot}72 KI$, at different temperatures, the results of which are recorded in the following table.

### TABLE XXXVIII.

$(468 - 4{\cdot}72z)\, H^2SO^4$, $4{\cdot}72\, \{(1 - z)\, KI + zHI\}$, $4{\cdot}72z KHSO^4$. Temperature $t^\circ$.

| $t = 10$, $y_0 = 7{\cdot}95$. | | $t = 15$, $y_0 = 8{\cdot}82$. | | $t = 20$, $y_0 = 9$. | |
|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 11′·77 | ·0114 | 7′·40 | ·0163 | 5′·02 | ·0234 |
| 13·65 | ·0114 | 8·39 | ·0163 | 5·74 | ·0232 |
| 16·18 | ·0114 | 9·71 | ·0163 | 6·59 | ·0234 |
| 19·75 | ·0114 | 11·59 | ·0163 | 7·85 | ·0232 |
| | | 14·15 | ·0164 | 9·59 | ·0232 |
| | | 18·50 | ·0164 | 12·33 | ·0233 |
| 63·38 | ·0114 | 26·93 | ·0163 | 17·39 | ·0233 |
| | | 48·63 | ·0164 | 29·82 | ·0233 |
| Mean rate . | ·0114 | Mean rate . | ·0163 | Mean rate . | ·0233 |

| $t = 20$, $y_0 = 8{\cdot}73$. | | $t = 25$, $y_0 = 8{\cdot}89$. | | $t = 30$, $y_0 = 10{\cdot}74$. | |
|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 5′·22 | ·0232 | 3′·64 | ·0327 | 2′·11 | ·0463 |
| 5·96 | ·0232 | 4·15 | ·0326 | 2·37 | ·0457 |
| 6·90 | ·0233 | 4·77 | ·0328 | 2·64 | ·0461 |
| 8·29 | ·0231 | 5·68 | ·0327 | 3·04 | ·0455 |
| 10·27 | ·0231 | (2) 16·17 | ·0324 | 3·52 | ·0457 |
| 13·48 | ·0231 | 13·03 | ·0325 | 4·17 | ·0459 |
| 19·70 | ·0231 | 22·93 | ·0327 | 5·15 | ·0459 |
| 37·60 | ·0232 | | | 6·80 | ·0457 |
| | | | | 10·00 | ·0455 |
| | | | | 18·56 | ·0460 |
| Mean rate . | ·0232 | Mean rate . | ·0326 | Mean rate . | ·0458 |

The experimental values of $\alpha$ in this table require no correction for expansion, the volume was made up to the same amount at each temperature, so that the only variable ingredient was water, less of which was contained in an unit volume at the higher temperatures than at the lower. No sensible departure from the law, due to this cause, can be detected. The most probable value of $m$ is $20{\cdot}35$ and of log $\alpha_0$

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$\bar{3}{\cdot}740$. The following table exhibits the agreement of the experimental and calculated numbers.

### TABLE XXXIX.

$(468 - 4{\cdot}72z)\ H^2SO^4$, $4{\cdot}72\ \{(1 - z)\ KI + zHI\}$, $4{\cdot}72zKHSO^4$. Temperature $t$° C.

| $t$. | log $\alpha$. | | $\alpha$. | |
|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. |
| 0 | | $\bar{3}{\cdot}740$ | | ·0055 |
| 10 | $\bar{2}{\cdot}057$ | $\bar{2}{\cdot}057$ | ·0114 | ·0114 |
| 15 | $\bar{2}{\cdot}212$ | $\bar{2}{\cdot}212$ | ·0163 | ·0163 |
| 20 | $\bar{2}{\cdot}366$ | $\bar{2}{\cdot}365$ | ·0233 | ·0232 |
| 25 | $\bar{2}{\cdot}514$ | $\bar{2}{\cdot}514$ | ·0326 | ·0326 |
| 30 | $\bar{2}{\cdot}661$ | $\bar{2}{\cdot}662$ | ·0458 | 0459 |

The number $m$ does not sensibly differ from the value 20·38 in all these three sets of experiments in which the main ingredient of the solution was hydrogen sulphate, although the ratio of the amount of $H^2SO^4$ to $KI$ varies from 99·2 to 27·9. Assuming the chemical change at zero centigrade in each set to be the unit change for that set, and the value of $m$ to be 20·38 for each set, the amount of chemical change, expressed in terms of the unit change, at a given temperature will be the same in all the three sets. In other words, if $\alpha_t$, $\alpha_0$ are the rates at $t$° and zero in any of the three sets, the ratio $\alpha_t : \alpha_0$ will be the same as the corresponding ratio in the other two sets; the theoretical value of this ratio being $\{(273 + t)/273\}^{20{\cdot}38}$, or $(T/T_0)^{20{\cdot}38}$.

In the following Table the values of log $(\alpha/\alpha_0)$ and of $\alpha/\alpha_0$, corresponding to each value of $t$ and log $(T/T_0)$, are given for the three sets of experiments, and also the calculated values of 20·38 log $(T/T_0)$ and of $(T/T_0)^{20{\cdot}38}$ compared with the values of log $(\alpha/\alpha_0)$ and of $\alpha/\alpha_0$ determined by experiment.

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## TABLE XL.

| *t*. | log (T/$T_0$) | log ($\alpha/\alpha_0$). | | | | $\alpha/\alpha_0$. | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Found. | | | Calculated. | Found. | | | Calculated. |
| | | 1. | 2. | 3. | | 1. | 2. | 3. | |
| 0 | ·0000 | 0·001 | .. | .. | 0·000 | 1·002 | .. | .. | 1·000 |
| 5 | ·0079 | 0·159 | .. | .. | 0·160 | 1·442 | .. | .. | 1·445 |
| 10 | ·0156 | 0·317 | .. | 0·316 | 0·318 | 2·075 | .. | 2·070 | 2·080 |
| 15 | ·0232 | 0·473 | .. | 0·473 | 0·473 | 2·972 | .. | 2·972 | 2·972 |
| 20 | ·0307 | 0·628 | 0·622 | 0·627 | 0·626 | 4·246 | 4·188 | 4·237 | 4·227 |
| 25 | ·0380 | 0·775 | .. | 0·775 | 0·775 | 5·957 | .. | 5·957 | 5·957 |
| 30 | ·0453 | 0·924 | 0·926 | 0·922 | 0·923 | 8·395 | 8·435 | 8·356 | 8·376 |
| 35 | ·0524 | 1·064 | .. | .. | 1·067 | 11·590 | .. | .. | 11·670 |
| 40 | ·0594 | 1·210 | 1·212 | .. | 1·210 | 16·220 | 16·290 | .. | 16·220 |
| 45 | ·0663 | 1·352 | .. | .. | 1·350 | 22·490 | .. | .. | 22·390 |
| 50 | ·0730 | 1·491 | 1·498 | .. | 1·488 | 30·970 | 31·480 | .. | 30·770 |

These numbers agree with one another and with the calculated values within the limits of experimental error. They are represented graphically on Diagram 5, fig. 1, p. 870, in the manner described on p. 861, and on Diagram 4, fig. 1, p. 864 in the manner described on p. 863, the points determined by experiment being in each case represented by crosses.

In all the sets of observations of the rates at different temperatures which we have thus far recorded and discussed the medium in which the change has taken place has been dilute sulphuric acid. The observations which follow show that in presence of hydrochloric acid the value of *m* is different, but that it is constant for all the cases in which the rates of change in this medium at different temperatures have been determined.

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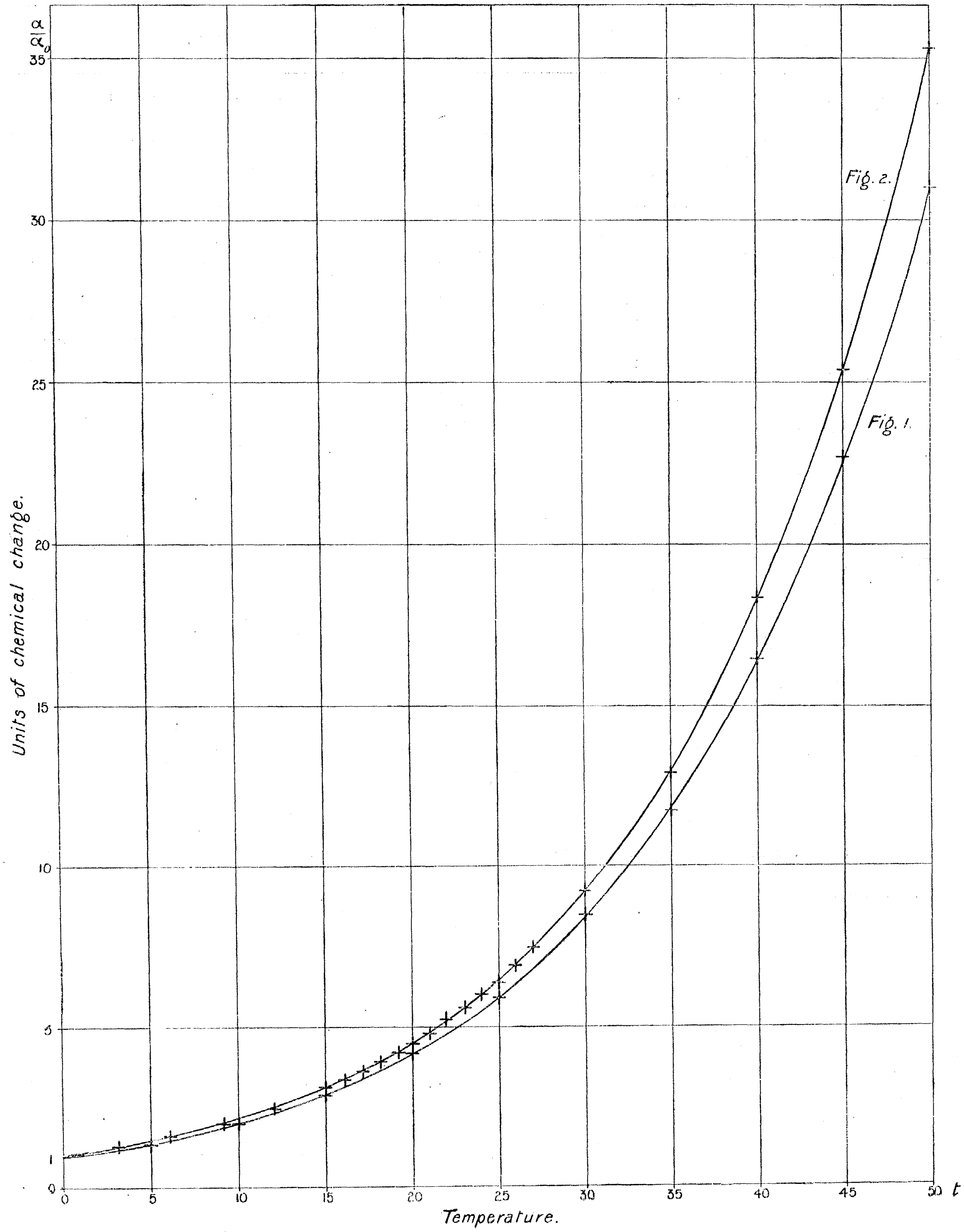
Diagram 5.



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The following Tables, XLI.–XLIV., give the conditions and results of these observations:—

## TABLE XLI.

$(381 - 7{\cdot}28z)\,HCl$, $7{\cdot}28\,\{(1-z)\,KI + zHI\}$, $7{\cdot}28zKCl$. Temperature $t°$ C.

| $t = 10{\cdot}11$, $y_0 = 17{\cdot}2$. | | $t = 15{\cdot}08$, $y_0 = 10{\cdot}2$. | | $t = 20{\cdot}34$, $y_0 = 6{\cdot}2$. | | $t = 25{\cdot}09$, $y_0 = 2{\cdot}2$. | |
|---|---|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 4′·52 | ·0132 | 5′·50 | ·0188 | 6′·47 | ·0272 | 16′·17 | ·0374 |
| 4·87 | ·0131 | 6·10 | ·0189 | 7·88 | ·0270 | 47·50 | ·0377 |
| 5·17 | ·0132 | 6·90 | ·0188 | 10·07 | ·0270 | | |
| 5·60 | ·0130 | | | | | | |
| 6·00 | ·0131 | | | | | | |
| 6·48 | ·0132 | | | | | | |
| Mean rate . | ·0131 | Mean rate . | ·0188 | Mean rate . | ·0271 | Mean rate . | ·0375 |

| $t = 18{\cdot}2$, $y_0 = 17{\cdot}2$. | | $t = 19{\cdot}28$, $y_0 = 10{\cdot}2$. | | $t = 20{\cdot}34$, $y_0 = 6{\cdot}2$. | | $t = 21{\cdot}32$, $y_0 = 17{\cdot}03$. | |
|---|---|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 2′·55 | ·0234 | 4′·05 | 0·255 | 6′·42 | ·0274 | 2′·07 | ·0292 |
| 2·72 | ·0234 | 4·52 | 0·255 | 7·85 | ·0272 | 2·20 | ·0293 |
| (2) 5·97 | ·0236 | 5·15 | 0·252 | 10·07 | ·0270 | | |
| 3·37 | ·0233 | | | | | | |
| 3·65 | ·0234 | | | | | | |
| Mean rate . | ·0234 | Mean rate . | ·0254 | Mean rate . | ·0272 | Mean rate . | ·0292 |

| $t = 22{\cdot}27$, $y_0 = 14{\cdot}03$. | | $t = 23{\cdot}2$, $y_0 = 11{\cdot}03$. | | $t = 24{\cdot}14$, $y_0 = 8{\cdot}03$. | | $t = 26{\cdot}13$, $y_0 = 5{\cdot}03$. | | $t = 27{\cdot}1$, $y_0 = 2{\cdot}03$. | |
|---|---|---|---|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 2′·33 | 0·318 | 2′·85 | ·0333 | 3′·73 | ·0356 | 5′·45 | ·0407 | 15′·43 | ·0439 |
| 2·58 | 0·309 | 3·15 | ·0333 | 4·37 | ·0352 | 7·05 | ·0405 | 67·13 | ·0437 |
| Mean rate ·0313 | | Mean rate ·0333 | | Mean rate ·0354 | | Mean rate ·0406 | | Mean rate 0·438 | |

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### TABLE XLII.

$(191 - 3{\cdot}64z)\ HCl$, $3{\cdot}64\ \{(1 - z)\ KI + zHI\}$, $3{\cdot}64zKCl$. Temperature $t°$ C.

| $t = 30{\cdot}05$, $y_0 = 17$. | | $t = 35{\cdot}05$, $y_0 = 10$. | | $t = 40{\cdot}05$, $y_0 = 6$. | |
|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 3′·85 | ·0157 | 4′·73 | ·0222 | 5′·85 | ·0313 |
| 4·12 | ·0157 | 5·33 | ·0221 | 7·17 | ·0311 |
| 4·42 | ·0157 | 6·00 | ·0222 | 9·32 | ·0310 |
| 4·68 | ·0158 | | | 13·15 | ·0309 |
| 5·03 | ·0159 | | | 22·02 | ·0316 |
| 5·57 | ·0156 | | | | |
| Mean rate . . | ·0157 | Mean rate . . | ·0222 | Mean rate . . | ·0312 |

### TABLE XLIII.

$(546 - 5{\cdot}21z)\ HCl$, $5{\cdot}21\ \{(1 - z)\ KI + zHI\}$, $5{\cdot}21zKCl$. Temperature $t°$ C.

| $t = 0$, $y_0 = 25{\cdot}25$. | | $t = 2{\cdot}98$, $y_0 = 21{\cdot}25$. | | $t = 5{\cdot}95$, $y_0 = 17{\cdot}25$. | |
|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 6′·80 | ·00594 | 6′·60 | ·00729 | 6′·43 | ·00929 |
| 7·18 | ·00586 | 6·92 | ·00731 | 6·88 | ·00923 |
| 7·47 | ·00589 | 7·18 | ·00743 | 7·40 | ·00918 |
| Mean rate . | ·00590 | Mean rate . | ·00734 | Mean rate . | ·00923 |

| $t = 8{\cdot}94$, $y_0 = 13{\cdot}25$. | | $t = 11{\cdot}96$, $y_0 = 9{\cdot}25$. | | $t = 15{\cdot}03$, $y_0 = 5{\cdot}25$. | |
|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 6′·85 | ·0115 | 7′·93 | ·0144 | 11′·75 | ·0180 |
| 15·47 | ·0115 | 8·92 | ·0145 | 14·95 | ·0179 |
| | | 10·27 | ·0144 | 20·40 | ·0180 |
| Mean rate . . | ·0115 | Mean rate . . | ·0144 | Mean rate . . | ·0180 |

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## TABLE XLIV.

$(273 - 5{\cdot}21z)\ HCl$, $5{\cdot}21\ \{(1 - z)\ KI + z\ HI\}$, $5{\cdot}21\ zKCl$. Temperature $t°$ C.

| $t = 15{\cdot}08$, $y_0 = 24{\cdot}13$. | | $t = 16{\cdot}07$, $y_0 = 19{\cdot}13$. | | $t = 17{\cdot}16$, $y_0 = 16{\cdot}13$. | | $t = 18{\cdot}2$, $y_0 = 13{\cdot}13$. | |
|---|---|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 4′·17 | ·01014 | 4′·98 | ·0108 | 5′·50 | ·0116 | 6′·27 | ·0126 |
| 4·53 | ·00975 | 5·27 | ·0108 | 5·87 | ·0116 | 6·77 | ·0127 |
| 4·65 | ·00996 | | | | | | |
| 4·85 | ·01000 | | | | | | |
| Mean rate . | ·00996 | Mean rate . | ·0108 | Mean rate . | ·0116 | Mean rate . | ·0126 |

| $t = 19{\cdot}28$, $y_0 = 10{\cdot}13$. | | $t = 20{\cdot}34$, $y_0 = 7{\cdot}13$. | | $t = 21{\cdot}32$, $y_0 = 4{\cdot}13$. | |
|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 7′·63 | ·0136 | 10′·25 | ·0148 | 17′·37 | ·0160 |
| 8·48 | ·0137 | 11·97 | ·0149 | 24·28 | ·0158 |
| | | | | 39·82 | ·0159 |
| Mean rate . . . | ·0136 | Mean rate . . . | ·0148 | Mean rate . . . | ·0159 |

The experimental numbers recorded in the preceding tables were corrected for expansion, and values of $\alpha$ calculated by interpolation to correspond to whole numbers of temperature. The value of $m$ in the formula $\alpha/\alpha_0 = (T/T_0)^m$ which most nearly satisfies the four sets of experimental values of $\alpha$, is 21·17.

The following tables, each of which corresponds to one of the preceding tables give the experimental and calculated values of log $\alpha$ and $\alpha$.

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## TABLE XLV.

$(381\cdot5 - 7\cdot29z)\,HCl$, $7\cdot29\,\{(1 - z)\,KI + zHI\}$, $7\cdot29\,zKCl$. Temperature $t°$ C.

| t. | Log. α. | | α. | |
|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. |
| 0 | | $\bar{3}$·774 | | ·00594 |
| 10 | $\bar{2}$·114 | $\bar{2}$·112 | ·0130 | ·0129 |
| 15 | $\bar{2}$·272 | $\bar{2}$·266 | ·0187 | ·0185 |
| 18 | $\bar{2}$·363 | $\bar{2}$·361 | ·0231 | ·0230 |
| 19 | $\bar{2}$·397 | $\bar{2}$·393 | ·0249 | ·0247 |
| 20 | $\bar{2}$·425 | $\bar{2}$·424 | ·0266 | ·0265 |
| 21 | $\bar{2}$·456 | $\bar{2}$·455 | ·0286 | ·0285 |
| 22 | $\bar{2}$·489 | $\bar{2}$·486 | ·0308 | ·0306 |
| 23 | $\bar{2}$·516 | $\bar{2}$·518 | ·0328 | ·0330 |
| 24 | $\bar{2}$·547 | $\bar{2}$·549 | ·0352 | ·0354 |
| 25 | $\bar{2}$·573 | $\bar{2}$·580 | ·0374 | ·0380 |
| 26 | $\bar{2}$·606 | $\bar{2}$·610 | ·0404 | ·0407 |
| 27 | $\bar{2}$·640 | $\bar{2}$·641 | ·0437 | ·0438 |

## TABLE XLVI.

$(191\cdot3 - 3\cdot64z)\,HCl$, $3\cdot64\,\{(1 - z)\,KI + zHI\}$, $3\cdot64\,zKCl$. Temperature $t°$ C.

| t. | Log. α. | | α. | |
|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. |
| 0 | | $\bar{3}$·240 | | ·00174 |
| 30 | $\bar{2}$·198 | $\bar{2}$·198 | ·0158 | ·0158 |
| 35 | $\bar{2}$·349 | $\bar{2}$·349 | ·0223 | ·0223 |
| 40 | $\bar{2}$·497 | $\bar{2}$·497 | ·0314 | ·0314 |

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## TABLE XLVII.

$(546{\cdot}8 - 5{\cdot}22z)\,HCl,\quad 5{\cdot}22\,\{(1-z)\,KI + zHI\},\quad 5{\cdot}22\,zKCl.$ Temperature $t^\circ$ C.

| *t*. | Log. *α*. | | *α*. | |
|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. |
| 0 | $\bar{3}{\cdot}770$ | $\bar{3}{\cdot}765$ | ·00589 | ·00582 |
| 3 | $\bar{3}{\cdot}866$ | $\bar{3}{\cdot}865$ | ·00734 | ·00733 |
| 6 | $\bar{3}{\cdot}966$ | $\bar{3}{\cdot}965$ | ·00925 | ·00923 |
| 9 | $\bar{2}{\cdot}062$ | $\bar{2}{\cdot}062$ | ·0115 | ·0115 |
| 12 | $\bar{2}{\cdot}159$ | $\bar{2}{\cdot}160$ | ·0144 | ·0144 |
| 15 | $\bar{2}{\cdot}254$ | $\bar{2}{\cdot}257$ | ·0179 | ·0181 |

## TABLE XLVIII.

$(273{\cdot}4 - 5{\cdot}22z)\,HCl,\quad 5{\cdot}22\,\{(1-z)\,KI + zHI\},\quad 5{\cdot}22\,zKCl.$ Temperature $t^\circ$ C.

| *t*. | Log. *α*. | | *α*. | |
|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. |
| 0 | | $\bar{3}{\cdot}507$ | | ·00321 |
| 15 | $\bar{3}{\cdot}995$ | $\bar{3}{\cdot}999$ | ·00989 | ·00998 |
| 16 | $\bar{2}{\cdot}030$ | $\bar{2}{\cdot}031$ | ·0107 | ·0107 |
| 17 | $\bar{2}{\cdot}061$ | $\bar{2}{\cdot}062$ | ·0115 | ·0115 |
| 18 | $\bar{2}{\cdot}096$ | $\bar{2}{\cdot}094$ | ·0125 | ·0124 |
| 19 | $\bar{2}{\cdot}127$ | $\bar{2}{\cdot}126$ | ·0134 | ·0134 |
| 20 | $\bar{2}{\cdot}160$ | $\bar{2}{\cdot}157$ | ·0144 | ·0143 |
| 21 | $\bar{2}{\cdot}191$ | $\bar{2}{\cdot}188$ | ·0152 | ·0154 |

In the following table the experimental values of log $(\alpha/\alpha_0)$ and $\alpha/\alpha_0$ are compared with the values calculated from the expressions $21{\cdot}17$ log. $(T/T_0)$ and $(T/T_0)^{21{\cdot}17}$ respectively.

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## TABLE XLIX.

| $t$. | log. $\frac{T}{T_0}$. | log. $\frac{\alpha}{\alpha_0}$. | | | | | $\frac{\alpha}{\alpha_0}$. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | XLV. | XLVI. | XLVII. | XLVIII. | Calculated. | XLV. | XLVI. | XLVII. | XLVIII. | Calculated. |
| 0 | ·0000 | .. | .. | ·005 | .. | ·000 | .. | .. | 1·01 | .. | 1·00 |
| 3 | ·0047 | .. | .. | ·101 | .. | ·100 | .. | .. | 1·26 | .. | 1·26 |
| 6 | ·0094 | .. | .. | ·201 | .. | ·200 | .. | .. | 1·59 | .. | 1·58 |
| 9 | ·0141 | .. | .. | ·297 | .. | ·298 | .. | .. | 1·98 | .. | 1·99 |
| 10 | ·0156 | ·340 | .. | .. | .. | ·338 | 2·19 | .. | .. | .. | 2·18 |
| 12 | ·0187 | .. | .. | ·394 | .. | ·395 | .. | .. | 2·48 | .. | 2·48 |
| 15 | ·0232 | ·498 | .. | ·489 | ·488 | ·492 | 3·15 | .. | 3·08 | 3·08 | 3·10 |
| 16 | ·0247 | .. | . | .. | ·523 | ·524 | .. | .. | .. | 3·33 | 3·34 |
| 17 | ·0262 | .. | .. | .. | ·554 | ·555 | .. | .. | .. | 3·58 | 3·59 |
| 18 | ·0277 | ·589 | .. | .. | ·589 | ·587 | 3·88 | .. | .. | 3·88 | 3·86 |
| 19 | ·0292 | ·623 | .. | .. | ·620 | ·619 | 4·20 | .. | .. | 4·17 | 4·16 |
| 20 | ·0307 | ·651 | .. | .. | ·653 | ·650 | 4·48 | .. | .. | 4·50 | 4·47 |
| 21 | ·0322 | ·682 | .. | .. | ·684 | ·681 | 4·81 | .. | .. | 4·83 | 4·80 |
| 22 | ·0337 | ·715 | .. | .. | .. | ·712 | 5·19 | .. | .. | .. | 5·15 |
| 23 | ·0351 | ·742 | .. | .. | .. | ·744 | 5·52 | .. | .. | .. | 5·55 |
| 24 | ·0366 | ·773 | .. | .. | .. | ·775 | 5·93 | .. | .. | .. | 5·96 |
| 25 | ·0380 | ·799 | .. | .. | .. | ·806 | 6·30 | .. | .. | .. | 6·40 |
| 26 | ·0395 | 832 | .. | .. | .. | ·836 | 6·80 | .. | .. | .. | 6·85 |
| 27 | ·0410 | ·866 | .. | .. | .. | ·867 | 7·35 | .. | .. | .. | 7·36 |
| 30 | ·0453 | .. | ·958 | .. | .. | ·958 | .. | 9·08 | .. | .. | 9·08 |
| 35 | ·0524 | .. | 1·109 | .. | .. | 1·109 | .. | 12·85 | .. | .. | 12·85 |
| 40 | ·0594 | .. | 1·257 | .. | .. | 1·257 | .. | 18·07 | .. | .. | 18·07 |

These numbers, which agree with each other and with the calculated values within the limits of experimental error, are represented graphically, in the two ways previously described, on Diagram 4, fig. 2, p. 864, and Diagram 5, fig. 2, p. 870.

The following table gives the results of a set of experiments made in a solution containing only hydrogen iodide.

## TABLE L.

21·8 *HI*. Temperature $t°$ C.

| $t$ = 20·03,<br>$y_0$ = 11·72. | | $t$ = 24·99,<br>$y_0$ = 7·72. | | $t$ = 30,<br>$y_0$ = 3·72. | |
|---|---|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 5·62 | ·0158 | 5·92 | ·0234 | 8·90 | ·0352 |
| 6·20 | ·0158 | 6·83 | ·0236 | 12·98 | ·0353 |
| 6·85 | ·0158 | 8·07 | ·0238 | 24·65 | ·0353 |
| Mean rate . | ·0158 | Mean rate . . | ·0236 | Mean rate . . | ·0353 |

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The values of $\alpha$ were corrected for expansion and values obtained by interpolation corresponding to whole numbers of temperature. The value of $m$ in the formula $\alpha/\alpha_0 = (T/T_0)^m$ is 24·1, and of log $\alpha_0$, 3·458. The following table exhibits the agreement of the found and calculated values of log $\alpha$ and $\alpha$.

TABLE LI.

| $t$. | Log $\alpha$. | | $\alpha$. | | Log $(\alpha/\alpha_0)$. | | $\alpha/\alpha_0$. | |
|---|---|---|---|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. | Found. | Calculated. | Found. | Calculated. |
| 0 | | $\bar{3}$·458 | | ·0029 | | ·000 | | 1·00 |
| 20 | $\bar{2}$·199 | $\bar{2}$·198 | ·0158 | ·0158 | ·740 | ·740 | 5·50 | 5·50 |
| 25 | $\bar{2}$·374 | $\bar{2}$·375 | ·0237 | ·0237 | ·916 | ·917 | 8·24 | 8·26 |
| 30 | $\bar{2}$·550 | $\bar{2}$·549 | ·0355 | ·0354 | 1·092 | 1·091 | 12·36 | 12 33 |

The numbers are represented graphically on Diagram 4, fig. 3, in the manner described on p. 863.

A comparison of this table with those on pp. 869 and 876 shows that the increase of the rates with temperature is much more rapid than in the cases in which the main ingredients were hydrogen sulphate and hydrogen chloride. At a temperature of 30° the ratio of the chemical change to that at zero is, in the case of hydrogen sulphate, 8·38, in the case of hydrogen chloride 9·08, and in the case of hydrogen iodide 12·33. The value of $m$ in the formula $\alpha/\alpha_0 = (T/T_0)^m$ depends upon the nature of the medium in which the chemical change takes place. This conclusion is confirmed by the results of a set of experiments made with a solution, into which were brought 273 $H^2SO^4$ and 190 $Na^2SO^4$. The observations are recorded in the following table.

Reserving the question of the probable interaction between hydrogen sulphate, potassium iodide, and sodium sulphate, the actual ingredients of the solution were, per cub. centim., 273 $H^2SO^4$, 5·21 $KI$, and 190 $Na^2SO^4$.

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TABLE LII.—Temperature $t°$ C.

| $t = 23$, $y_0 = 11{\cdot}67$. | | $t = 33$, $y_0 = 5{\cdot}67$. | |
|---|---|---|---|
| Intervals. | $\alpha$. | Intervals. | $\alpha$. |
| 6·12 | ·0147 | 7·33 | ·0264 |
| 6·80 | ·0144 | 9·03 | ·0267 |
| 7·58 | ·0144 | 12·07 | ·0263 |
| 8·37 | ·0146 | | |
| 9·58 | ·0146 | | |
| Mean rate . . | ·0145 | Mean rate . . | ·0265 |

The value of $m$ deduced from the rates in this table is 18·1. The ratio of the rate at a temperature of 30° to that at zero is 6·58, which is much less than 8·38, the corresponding ratio in a medium containing only hydrogen sulphate. This variation may probably be due to a change in the actual substances in the solution. At 23° the solution contained

$$(273 - 190y)\, H^2SO^4 + 380y NaHSO^4 + 190\,(1 - y)\, Na^2SO^4.$$

The value of $y$, that is the equilibrium between the hydrogen sulphate, the sodium hydrogen sulphate, and the sodium sulphate in the solution, is likely to change with rise of temperature, the amount of sodium hydrogen sulphate probably increasing and that of hydrogen sulphate and of sodium sulphate decreasing correspondingly.

The value of $m$ in the formula $\alpha/\alpha_0 = (T/T_0)^m$ is less for solutions containing sodium hydrogen carbonate than any of the values hitherto found. An approximation to the value can be obtained from the results of the experiments recorded on p. 848, with 57·2 $NaHCO^3$ and 8·07 $NaI$, at a temperature of 17°. The rate with unit of iodide is $2670 \times 10^{-6}$, and the rate with the same amounts of $NaHCO^3$ and $NaI$ at a temperature of 15° deduced from the formula (24), p. 847, is $2480 \times 10^{-6}$. The value of $m$ deduced from the equation, $\log(2670/2480) = m \log\{(273 + 17)/(273 + 15)\}$, is 10·7. Another approximation can be obtained from the value of the increment of the rate per unit of $NaHCO^3$ found on p. 851. The value of this increment at a temperature of 19° is $45{\cdot}5 \times 10^{-6}$, but at a temperature of 15° (p. 847) it is $40 \times 10^{-6}$. The value of $m$, deduced from the equation,

$$\log(45{\cdot}5/40) = m \log\{(273 + 19)/(273 + 15)\} \quad . \quad . \quad . \quad . \quad (48),$$

is 9·3. The mean of these two values, viz., 10, may be taken as an approximation to the value of $m$ in solutions whose main ingredient is sodium hydrogen carbonate.

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The following table gives a comparison of the effect of temperature in solutions containing mainly $NaHCO^3$, $H^2SO^4$, HCl, and HI. The rate at zero centigrade is in each case taken to be unity.

TABLE LIII.

| *t.* | $NaHCO^3$.<br>$m = 10$. | $H^2SO^4$.<br>$m = 20·4$. | HCl.<br>$m = 21·2$. | HI.<br>$m = 24·1$. |
|---|---|---|---|---|
| | | $\alpha$. | | |
| 0 | 1·00 | 1·00 | 1·00 | 1·00 |
| 10 | 1·43 | 2·08 | 2·18 | 2·38 |
| 20 | 2·03 | 4·23 | 4·47 | 5·50 |
| 30 | 2·84 | 8·38 | 9·08 | 12·33 |
| 40 | 3·93 | 16·22 | 18·07 | 27·04 |

A further confirmation of the law of connexion between chemical change and temperature is obtained from experiments on the rate of change of hydrogen chlorate and potassium iodide, by W. H. PENDLEBURY and M. SEWARD, in vol. 45 of the 'Proceedings of the Royal Society.' On p. 420 are given the rates at different temperatures. In the following table are given these rates and their values calculated from the formula

$$\log (\alpha/\alpha_0) = 40·5 \log (T/T_0) \; . \; . \; . \; . \; . \; . \; . \; . \; (49).$$

TABLE LIV.

| *t.* | $\alpha$. | | $\alpha/\alpha_0$. | |
|---|---|---|---|---|
| | Found. | Calculated. | Found. | Calculated. |
| 4 | ·00136 | ·00139 | 1·76 | 1·80 |
| 7 | ·00213 | ·00215 | 2·74 | 2·79 |
| 10 | ·00330 | ·00324 | 4·27 | 4·20 |
| 13 | ·00509 | ·00498 | 6·59 | 6·44 |
| 15 | ·00215 | ·00212 | 8·83 | 8·73 |
| 20 | ·00427 | ·00427 | 17·60 | 17·50 |
| 20 | ·00143 | ·00142 | 17·60 | 17·50 |
| 21 | ·00164 | ·00163 | 20·30 | 20·20 |
| 22 | ·00186 | ·00187 | 23·00 | 23·10 |
| 23 | ·00213 | ·00214 | 26·30 | 26·50 |
| 25 | ·00838 | ·00840 | 34·50 | 34·50 |
| 30 | ·01641 | ·01660 | 67·50 | 68·20 |

The values of $\alpha$ found agree on the whole with the calculated values within the limits of experimental error. The value of $m$ in the case of the decomposition

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of hydrogen chlorate at different temperatures is twice as great as in the case of the reaction between hydrogen dioxide and hydrogen iodide in the presence of hydrogen sulphate. Hence, as in the latter case the rate is approximately doubled by a rise in temperature of 10°, it is approximately doubled in the former case by a rise of 5°.

In the discussion of their results the authors adopted a view of the relation between chemical change and temperature, which was originally taken by us, but which we were led to reject for reasons given on p. 859 of this paper.

### *Discussion of the Preceding Results.*

It has been shown, p. 842, that in a medium consisting of water and hydrogen iodide the amount of which in a cubic centimeter varies between 14·5 *HI* and 43·5 *HI*, the rate of change $\alpha$ is given by the formula $\alpha = i\,\{a + b\,(i - 1)\}$, $i$ being the number of *HI* in a cubic centimeter, $a$ the rate when one *HI* is present and $b$ the increment of $a$ per unit substitution for water of *HI*. Both $a$ and $b$ remain constant in a set of experiments made at the same temperature but vary with the temperature according to the law $a_1 = a_0\,(\mathrm{T}_1/\mathrm{T}_0)^{24 \cdot 1}$, $b_1 = b_0\,(\mathrm{T}_1/\mathrm{T}_0)^{24 \cdot 1}$, $a_1$, $b_1$ being the values of $a$ and $b$ at an absolute temperature $\mathrm{T}_1$, and $a_0$, $b_0$ their values at a temperature $\mathrm{T}_0$; see p. 877. The most probable values of $a$ and $b$ at a temperature of 30° C. or 303° absolute are $1210 \times 10^{-6}$ and $19 \cdot 4 \times 10^{-6}$ respectively, so that the formula for $\alpha$ at a temperature 30° C. with a given number $i$ of *HI* is

$$\alpha = i\,\{1210 + 19 \cdot 4\,(i - 1)\}\,10^{-6} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50).$$

On pp. 830 and 837 the results of three sets of experiments with 14·22 *HI* are given in which $\alpha$ has the values ·0210, ·0208, ·0214; the formula gives the value ·0209, which agrees with the mean of the experimental values within the usual limit of error of 1 per cent. On p. 841 the rate with 14·5 *HI* is ·0214, the formula gives ·0213; on p. 876 the rate with 21·8 *HI* is ·0353, the formula gives ·0351.

At a temperature of 20° C. or 293° absolute, the value of $a$ is $1210 \times (\frac{293}{303})^{24 \cdot 1} = 540$, and of $b$, $19 \cdot 4 \times (\frac{293}{303})^{24 \cdot 1} = 8 \cdot 65$, so that the formula for the rate with $i$ *HI* at 20° C. is

$$\alpha = i\,\{540 + 8 \cdot 65\,(i - 1)\}\,10^{-6} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (51).$$

On p. 833 the rate with 22·82 *HI* at 20° C. is ·0167, the formula gives ·0166; on p. 876 the rate with 21·8 *HI* at 20° C. is ·0158, the formula gives ·0157; these values agree within the limit of experimental error. It will be observed that in all these comparisons the calculated results fall slightly below the observed values; the reason for this is that no account is taken of the small additions of hydrogen sulphate introduced into the solution with the hydrogen dioxide.

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These comparisons of calculated and observed values of the rate of the chemical changes here considered justify the conclusion that the rate at an absolute temperature $T_1$ with $i$ $HI$ is given by the formula $i\{a_1 + b_1(i-1)\}$ and the rate at an absolute temperature $T_2$ by the formula $i\{a_1 + b_1(i-1)\}(T_2/T_1)^m$ where the value of $m$ is 24·1, and that at a temperature of 30° C. or 303° absolute, the values of $a$ and $b$ are $1210 \times 10^{-6}$ and $19{\cdot}4 \times 10^{-6}$ respectively. The formula at zero or 273° absolute, may be deduced from formula (50) by means of the equation $\alpha_1 = \alpha_0(T_1/T_0)^{24{\cdot}1}$. This formula is

$$i\{98 + 1{\cdot}57(i-1)\}\,10^{-6} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52),$$

and the formula at any temperature $t$ is

$$i\{98 + 1{\cdot}57(i-1)\}\,10^{-6} \times \left(\frac{273+t}{273}\right)^{24{\cdot}1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (53).$$

We have seen that, at the three different temperatures of 16°, 20°, and 30° C., the law of variation of the rate with hydrogen sulphate, in a medium consisting mainly of water and hydrogen sulphate at a given temperature, is given by the formula

$$\alpha = i\{c_1 + d_1(s - s_1)\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (54),$$

where $s$ varies between the limits $s_1$ and $s_2$, and by the formula

$$\alpha = i\{c_2 + d_2(s - s_2)\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (55),$$

where $s$ varies between the limits $s_2$ and $s_3$; and the explanation given of the different values of $d_1$ and $d_2$ is that between the limits $s_1$ and $s_2$ two hydrates are present. The hydrate corresponding to $s_1$ continually diminishes, and the hydrate corresponding to $s_2$ continually increases, as $s$ increases between these limits, until the limit $s_2$ is reached, at which point the medium consists entirely of the hydrate corresponding to $s_2$. A further increase in $s$ diminishes the hydrate corresponding to $s_2$, and increases the hydrate corresponding to $s_3$, and so on. On this hypothesis, suppose $d_0$ to be the increase of rate per unit of the first hydrate formed, $d_1$ the increase of rate per unit of decrease of the first hydrate and increase of the second, and so on. The formula for the rate from $s = 0$ to $s = s_1$ is of the form,

$$\alpha = i\{c_0 + d_0 s\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (56),$$

and this formula will be valid until $s = s_1$, at which point the rate is

$$\alpha_1 = i(c_0 + d_0 s_1) = ic_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (57).$$

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From $s = s_1$ to $s = s_2$ the formula will become

$$\alpha = i\{c_1 + d_1(s - s_1)\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (58),$$

which will hold good until $s = s_2$, when the rate is

$$\alpha_2 = i\{c_1 + d_1(s_2 - s_1)\} = ic_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (59).$$

Proceeding in the same manner, the formula from $s = s_{r-1}$ to $s = s_r$ is

$$\alpha = i\{c_{r-1} + d_{r-1}(s - s_{r-1})\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

where

$$c_{r-1} = c_{r-2} + d_{r-2}(s_{r-1} - s_{r-2}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (61);$$

hence the final formula which is valid between the values $s_{r-1}$ and $s_r$ is

$$\alpha = i\{c_0 + d_0 s_1 + d_1(s_2 - s_1) + d_2(s_3 - s_2) + \ldots + d_{r-1}(s - s_{r-1})\} \,. \quad (62).$$

This formula may be also written in the form

$$\begin{aligned}\alpha &= i\{c_0 + (d_0 - d_1)s_1 + (d_1 - d_2)s_2 + \ldots + (d_{r-2} - d_{r-1})s_{r-1} + d_{r-1}s\} \\ &= i(c'_{r-1} + d_{r-1}s) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (63),\end{aligned}$$

which shows that if $d_0, d_1 \ldots d_{r-1}$ are in ascending order of magnitude, the quantity $c'_{r-1}$ may become negative; but if they are in descending order of magnitude $c'_{r-1}$ is always positive. There is reason pp. 831, 836, to believe that at first they are in descending order, and finally in ascending order, so that at some value of $s_r$, $c'_{r-1}$ may become nearly equal to $c_0$.

If a definite hydrate $n_1 H^2O,H^2SO^4$ is formed when $s = s_1$, and another $n_2 H^2O,H^2SO^4$ when $s = s_2$, and if $h_1$, $h_2$ are the quantities of $H^2O$ present when these hydrates are formed, these quantities being with sufficient accuracy assumed to be $h - \mu s_1$, $h - \mu s_2$, the amounts $x$ and $y$ of the first and second hydrate are given by the equation

$$\left.\begin{aligned} n_1 x + n_2 y &= h - \mu s \\ x + y &= s \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (64),$$

hence

$$x = (h - \mu s - n_2 s)/(n_1 - n_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (65),$$

$$y = (n_1 s - h + \mu s)/(n_1 - n_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (66),$$

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and if $e_1$, $e_2$ are the increments of unit rate per unit of the hydrates, the rate between $s = s_1$, and $s = s_2$ is given by the formula

$$\alpha = i\,\{f_1 + e_1 x + e_2 y\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (67),$$

$$= i\,[f_1 - (e_2 - e_1)\,h/(n_1 - n_2) + \{\mu\,(e_2 - e_1) + n_1 e_2 - n_2 e_1\} s/(n_1 - n_2)] \quad . \quad (68).$$

Comparing this with the formula (54) we obtain

$$d_1 = \{\mu\,(e_2 - e_1) + n_1 e_2 - n_2 e_1\}/(n_1 - n_2) \quad . \quad . \quad . \quad . \quad . \quad (69),$$

$$c_1 = f_1 - (e_2 - e_1)\,h/(n_1 - n_2) + d_1 s_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (70),$$

from which, if the hydrates $n_1$, $n_2$ were known, and their increments $e_1$, $e_2$ of unit rate, the increment $d_1$ could be calculated.

Until the first hydrate ascertained corresponding to $s_1\ H^2SO^4$ is reached, the formula for $\alpha$ with $s\ H^2SO^4$, and $i\ HI$ is at a temperature $t_1$,

$$\alpha = i\{a + b\,(i - 1) + d_1 s\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (71);$$

when $s = s_1$, this becomes

$$\alpha_1 = i\{a + b\,(i - 1) + d_1 s_1\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (72).$$

For values of $s$ between $s_1$ and $s_2$, the value of $s$ corresponding to the second hydrate ascertained,

$$\alpha = i\{a + b\,(i - 1) + d_1 s_1 + d_2\,(s - s_1)\} \quad . \quad . \quad . \quad . \quad . \quad (73);$$

when $s = s_2$, this becomes

$$\alpha_2 = i\{a + b\,(i - 1) + d_1 s_1 + d_2\,(s_2 - s_1)\} \quad . \quad . \quad . \quad . \quad . \quad (74).$$

For values of $s$ beyond this second hydrate,

$$\alpha = i\{a + b\,(i - 1) + d_1 s_1 + d_2\,(s_2 - s_1) + d_3\,(s - s_2)\} \quad . \quad . \quad (75).$$

The results of the experiments on the variation of rate with temperature show that for any other temperature $t$ the rates corresponding to these are obtained by multiplying them by the factor $\{(273 + t)/(273 + t_1)\}^m$.

The values assumed in the following discussion for the constants in these formulæ are at a temperature of 30°

$b = 19{\cdot}4 \times 10^{-6}$, previously ascertained (p. 880),

$d_1 = 18{\cdot}1 \times 10^{-6}$, obtained as a mean of the values of $d$, at the temperatures 16°, 20°, 30°, previously employed in the discussion of the experiments on pp. 822 to 836.

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$d_2 = 22{\cdot}4 \times 10^{-6}$, similarly obtained,
$d_3 = 26{\cdot}5 \times 10^{-6}$, also similarly obtained,
$s_1 = 515$, corresponding to the hydrate $H^2SO^4, 106H^2O$,
$s_2 = 762$, ,, ,, ,, $H^2SO^4, 71H^2O$,

values already determined in the same sets of experiments,

$m = 20{\cdot}38$, determined from the experiments on temperature.

The value of $a$ has now to be found. Substituting the values of the constants assumed above in the whole series of experiments in which hydrogen sulphate is a main ingredient of the solution, we obtain the following table; the first column gives the amount and nature of the iodide used, the second the number $n$ of experiments which give the value of $a \times 10^6$, given in the third column. The fourth column is the product $na \times 10^6$. The true value of $a \times 10^6$ is finally obtained by dividing the sum of the numbers $na \times 10^6$ by the sum of the numbers $n$. An examination of the values of $a$ shows that the value of $a$ corresponding to $i = 22{\cdot}82$ falls considerably below the mean value of the rest. This value is excluded from the computation. In the set of experiments from which this value is found, the ratio of the number $s$ of $H^2SO^4$ to the number $i$ of $HI$ is at first 2 and finally 12, and it appears hereafter that in a medium of water, hydrogen sulphate, and hydrogen iodide, in which the ratio $s : i$ falls below 20, the constant $b$ has a smaller value than it has in media in which the hydrogen sulphate predominates, and that the value of the temperature-constant $m$ has some value intermediate between 24·1 and 20·38 which are its values when the solution consists mainly of hydrogen iodide and hydrogen sulphate respectively.

TABLE LV.

| $i$. | $n$. | $a \times 10^6$. | $na \times 10^6$. |
|---|---|---|---|
| *KI.* | | | |
| 3·64 | 8 | 1220 | 9760 |
| 3·64 | 5 | 1230 | 6150 |
| 3·64 | 3 | 1240 | 3720 |
| 4·72 | 1 | 1190 | 1190 |
| 7·29 | 1 | 1180 | 1180 |
| 3 64 | 1 | 1290 | 1290 |
| 3·64 | 1 | 1220 | 1220 |
| 7·29 | 1 | 1220 | 1220 |
| 4·72 | 1 | 1220 | 1220 |
| *HI* | | | |
| 12·2 | 6 | 1210 | 7260 |
| 12·2 | 3 | 1175 | 3525 |
| 12·2 | 5 | 1250 | 6250 |
| 11·41 | 7 | 1265 | 8855 |
| 11·41 | 2 | 1250 | 2500 |
| | 45 | 1230 | 55340 |

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Assuming the value of $a \times 10^6$ at a temperature 30° to be 1230, its value at zero is 147; and the values of $b$, $d_1$, $d_2$, $d_3$ at zero are, when multiplied by the factor $10^6$, 2·32, 2·16, 2·68, 3·16 respectively, so that the formulæ for $\alpha$ at zero, corresponding to the general formulæ 71, 73, 75, are

$$\alpha = i\{147 + 2{\cdot}32(i-1) + 2{\cdot}16s\}10^{-6} \quad \text{(76)},$$

$$\alpha = i\{147 + 2{\cdot}32(i-1) + 2{\cdot}16 \times 515 + 2{\cdot}68(s-515)\}10^{-6} \quad \text{(77)},$$

$$\alpha = i\{147 + 2{\cdot}32(i-1) + 2{\cdot}16 \times 515 + 2{\cdot}68(762-515) + 3{\cdot}16(s-762)\}10^{-6} \quad \text{(78)},$$

and the formulæ corresponding to these at a temperature $t$ are obtained by multiplying these by the factor $\{(273+t)/273\}^{20{\cdot}38}$.

At a temperature of 16° the three formulæ are

$$\alpha = i\{469 + 7{\cdot}4(i-1) + 6{\cdot}89s\}10^{-6} \quad \text{(79)},$$

$$\alpha = i\{469 + 7{\cdot}4(i-1) + 6{\cdot}89 \times 515 + 8{\cdot}55(s-515)\}10^{-6} \quad \text{(80)},$$

$$\alpha = i\{469 + 7{\cdot}4(i-1) + 6{\cdot}89 \times 515 + 8{\cdot}55(762-515) + 10{\cdot}09(s-762)\}10^{-6} \quad \text{(81)}.$$

At a temperature of 20° they are

$$\alpha = i\{621 + 9{\cdot}8(i-1) + 9{\cdot}13s\}10^{-6} \quad \text{(82)},$$

$$\alpha = i\{621 + 9{\cdot}8(i-1) + 9{\cdot}13 \times 515 + 11{\cdot}32(s-515)\}10^{-6} \quad \text{(83)},$$

$$\alpha = i\{621 + 9{\cdot}8(i-1) + 9{\cdot}13 \times 515 + 11{\cdot}32(762-515) + 13{\cdot}37(s-762)\}10^{-6} \quad \text{(84)}.$$

At a temperature of 30° they are

$$\alpha = i\{1230 + 19{\cdot}4(i-1) + 18{\cdot}1s\}10^{-6} \quad \text{(85)},$$

$$\alpha = i\{1230 + 19{\cdot}4(i-1) + 18{\cdot}1 \times 515 + 22{\cdot}4(s-515)\}10^{-6} \quad \text{(86)},$$

$$\alpha = i\{1230 + 19{\cdot}4(i-1) + 18{\cdot}1 \times 515 + 22{\cdot}4(762-515) + 26{\cdot}5(s-762)\}10^{-6} \quad \text{(87)}.$$

These formulæ give values of $\alpha$ which agree within the limits of experimental error with all the values of $\alpha$ recorded in the preceding pages, with the exception of (1) those in which $i = 11{\cdot}41$, and $s$ has values ranging from 44 to 219; (2) those in which $i = 12{\cdot}2$, and $s$ has values ranging from 54 to 218; (3) those in which

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$i = 22{\cdot}82$, and $s$ has values ranging from 44 to 263. In all these cases the ratio of $s$ to $i$ falls below 20. The values of $\alpha$ are given within the limits of experimental error if the values of $b$, the increment per unit of iodide, at different temperatures, are assumed to follow the law $b_1 = b_0\,(T_1/T_0)^{24{\cdot}1}$, instead of the law $b_1 = b_0\,(T/T_0)^{20{\cdot}38}$. In the absence of experiments which would show the law of variation of $m$ in the formula $\alpha_1 = \alpha_0\,(T/T_0)^m$, with the amounts of water, hydrogen iodide, and hydrogen sulphate present in the medium, this assumption gives a sufficient approximation to the actual state of the case.

The values of $b$ at 16° and 20° on this assumption are $19{\cdot}4\ (289/303)^{24{\cdot}1} = 6{\cdot}21$, and $19{\cdot}4\,(293/303)^{24{\cdot}1} = 8{\cdot}65$.

At 16° the formula is

$$\alpha = i\,\{469 + 6{\cdot}21\,(i - 1) + 6{\cdot}89s\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (88).$$

At 20° the formula is

$$\alpha = i\,\{621 + 8{\cdot}65\,(i - 1) + 9{\cdot}13s\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (89).$$

These formulæ are approximately true for values of $i$ between 11 and 23, and for values of $s$ between 44 and $20i$.

In a medium consisting of water, hydrogen iodide and hydrogen chloride, the formula for the rate at a temperature $t_1$ is of the form

$$\alpha = i\,\{a + b\,(i - 1) + ec\}$$

$i$ and $c$ being the number of $HI$ and $HCl$ present in the solution. The rate at another temperature $t$ is obtained by multiplying by the factor $\{(273 + t)/(273 + t_1)\}^{21{\cdot}17}$.

When the iodide is in the form $iKI$, and the assumption is made that $iHI$ is produced at the expense of $iHCl$, the formula becomes

$$\alpha = i\,\{a + b\,(i - 1) + e\,(c - i)\}.$$

Assuming further that the value of $b$ at a temperature 30° is $19{\cdot}4 \times 10^{-6}$ as in the case of media consisting of water and hydrogen iodide or of water, hydrogen iodide and hydrogen sulphate, the value of $e$, the increment per unit of hydrogen chloride per unit of hydrogen iodide, which satisfies the values of $\alpha$ obtained in the experiments recorded on p. 840, and in those made at various temperatures recorded on pp. 874, 875, is $16{\cdot}2 \times 10^{-6}$; and the mean value of $a$ determined in the same manner as in the case of hydrogen sulphate is $1230 \times 10^{-6}$. It is seen that this value of $a$ is the same for solutions containing hydrogen chloride as it is for solutions containing hydrogen sulphate.

In all the experiments from which these values of $a$ and $e$ are determined, the values of $i$ range from 3·64 to 14·56, and the values of $c$ range from 191·3 to 381·3,

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The ratio $c:i$ exceeds in all cases the value 25. Within these limits the formula for $\alpha$ at 30° is

$$\alpha = i\,\{1230 + 19{\cdot}4\,(i - 1) + 16{\cdot}2c\}\,10^{-6} \quad . \quad . \quad . \quad . \quad . \quad (90).$$

The corresponding formula at zero is

$$\alpha = i\,\{135 + 2{\cdot}14\,(i - 1) + 1{\cdot}78c\}\,10^{-6} \quad . \quad . \quad . \quad . \quad . \quad (91),$$

and the corresponding formula at a temperature $t$ is obtained by multiplying by the factor $\{(273 + t)/273\}^{21{\cdot}17}$.

In the experiments recorded on p. 837 with 14·22 $HI$, and with numbers of $HCl$, ranging from 71·1 to 355·5, the value of $e$ is $16{\cdot}8 \times 10^{-6}$, a value higher than $16{\cdot}2 \times 10^{-6}$, the value which satisfies the experiments discussed above, and the value of $a$ is also larger, being $1345 \times 10^{-6}$ instead of $1230 \times 10^{-6}$. It is also seen that the value of $e$ for the range of numbers of $HCl$ from 0 to 71·1 is $18 \times 10^{-6}$ instead of $16{\cdot}8 \times 10^{-6}$. An examination of Table XIV. shows that the value of $e$ between 284·4 $HCl$ and 355·5 $HCl$ falls below the values of $e$ for the range 71·1 $HCl$ to 284·4 $HCl$. It seems probable that in media consisting of water, hydrogen iodide, and hydrogen chloride, in which the ratio $c:i$ falls below 20, the values of $a$ and $e$ are greater than in similar media in which the ratio of $c:i$ is greater than 20. The same kind of difference in the values of $a$ and $d$ has already been observed in the case of media consisting of water, hydrogen iodide, and hydrogen sulphate in which the ratio $s:i$ is less than 20. Further experiments are needed to reveal the cause of this variation in the values of these constants.

An examination of these cases of chemical action in media, the constituents of which are varied, leads to the conclusion that the rate of action at a given temperature $t_1$, in a medium consisting of water, hydrogen iodide, and another substance X, is given by the equation

$$\alpha_1 = i\,\{a_1 + b_1\,(i - 1) + c_1x\},$$

where $i$ is the number of $HI$, $x$ the number of $X$ in an unit volume, and $a_1$, $b_1$, $c_1$ are constants, provided that the ratio $x:i$ is sufficiently great to make the medium homogeneous throughout the range of the values of $x$. The rate of action at another temperature $t_2$ is, under the same conditions,

$$\alpha_2 = i\,\{a_2 + b_2\,(i - 1) + c_2x\},$$

$a_2$, $b_2$, $c_2$ being constants connected with $a_1$, $b_1$, $c_1$ by the equations,

$$a_2/a_1 = b_2/b_1 = c_2/c_1 = (T_2/T_1)^m,$$

$m$ being a constant depending only upon the nature of the medium.

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## APPENDIX.

### *On Chemical Equilibrium.*

The case of reverse action discussed in pp. 854, 855 is one which is probably of frequent occurrence, and deserves a special investigation. The general problem may be thus stated.

In a homogeneous medium two substances AB, CD interact to form the two AC, BD, which also interact to re-form the first pair; the amount of AC formed per unit of time varies as the amount of AB when CD is constant, and the same law governs the action of the other substances; having given the amount of each substance present at a given time, to determine the amount present at any subsequent time.

Let $a$, $a'$, $b$, $b'$ be the initial amounts of AB, CD, AC, BD respectively, and $x$, $x'$, $y$, $y'$ the corresponding amounts at a subsequent time $t$; these quantities are connected by the equations $x + y = a + b$, $x + y' = a + b'$, $x' + y = a' + b$, $x' + y' = a' + b'$, so that $\dot{x} = \dot{x}' = -\dot{y} = -\dot{y}'$. If, when an unit of each of the substances AB, CD is constantly present, $\alpha$ of each of them undergoes change in an unit of time, and $\beta$ is a similar quantity for AC, BD, the law of chemical change above given leads to the equation,

$$\begin{aligned}\dot{x} &= \beta yy' - \alpha xx' \\ &= \beta\,(a + b - x)\,(a + b' - x) - \alpha x\,(a' - a + x), \\ &= \beta\,\{bb' - (b + b')\,(x - a) + (x - a)^2\} \\ &\quad - \alpha\,\{aa' + (a + a')\,(x - a) + (x - a)^2\}.\end{aligned}$$

Putting

$$\lambda = 4\,(\beta - \alpha)\,(\beta bb' - \alpha aa'),$$

$$\mu = \alpha\,(a + a') + \beta\,(b + b'),$$

and

$$\nu^2 = \mu^2 - \lambda = \{(a - a')\,\alpha + (b - b')\,\beta\}^2 + 4\,\alpha\beta\,(a + b)\,(a' + b'),$$

the equation becomes

$$4\,(\beta - \alpha)\,(x - a)^{\cdot} = 2\,\{(\beta - \alpha)\,(x - a) - \mu\}^2 - \nu^2;$$

the solution of which is

$$\log\left[\left\{\frac{2\,(\beta - \alpha)\,(x - a) - \mu - \nu}{2\,(\beta - \alpha)\,(x - a) - \mu + \nu}\right\}\frac{\mu - \nu}{\mu + \nu}\right] = \nu t,$$

or

$$2\,(\beta - \alpha)\,(x - a) = (\mu + \nu)\,\frac{1 - e^{\nu t}}{1 - \dfrac{\mu + \nu}{\mu - \nu}\,e^{\nu t}};$$

putting

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$$(\mu+\nu)\,/\,2\,(\beta-\alpha)=c,$$
$$(\mu+\nu)\,/\,(\mu-\nu)=k,$$
$$x=a+c\,(1-e^{\nu t})\,/\,(1-ke^{\nu t}).$$

It follows that if $u=c\,(1-e^{\nu t})\,/\,(1-ke^{\nu t})$ the quantities of AB, CD, AC, BD present at a time $t$, are respectively $a+u$, $a'+u$, $b-u$, $b'-u$; $u$ being a positive or negative quantity.

When $t$ is infinite,

$$u=c/k=(\mu-\nu)\,/\,2\,(\beta-\alpha),$$

and

$$\begin{aligned}4\,(\beta-\alpha)\,(\beta yy'-\alpha xx')&=4\,(\beta-\alpha)\,\{\beta\,(b-u)\,(b'-u)-\alpha\,(a+u)\,(a'+u)\}\\&=\lambda-4\,(\beta-\alpha)\,\mu u+4\,(\beta-\alpha)^2\,u^2\\&=\lambda-2\mu\,(\mu-\nu)+(\mu-\nu)^2\\&=\lambda-\mu^2+\nu^2=0.\end{aligned}$$

So that theoretically after an infinite time chemical equilibrium is established, the quantities of AB, CD, AC, BD constantly present being respectively $a+c/k$, $a'+c/k$, $b-c/k$, $b'-c/k$.

We may, without loss of generality, consider $\beta$ to be greater than $\alpha$, so that $c$ is positive, and the sign of $k$ depends on that of $\mu-\nu$ or $\lambda$. Now $\lambda$ is positive or negative according as $\beta bb'-\alpha aa'$ is positive or negative, *i.e.*, according as the amount of AB is initially increasing or diminishing. If $k$ is negative, say $-k'$, the equation for the amount of AB at a time $t$ is

$$x=a-c\,\frac{e^{\nu t}-1}{k'e^{\nu t}+1},$$

and when equilibrium is established the amounts of AB, CD, AC, BD present are respectively $a-c/k'$, $a'-c/k'$, $b+c/k'$, $b'+c/k'$.

In the particular case when $\alpha=\beta$

$$\begin{aligned}x&=a+\frac{bb'-aa'}{a+a'+b+b'}\,\{1-e^{-(a+a'+b+b')\,\alpha t}\}\\&=\frac{(a+b)\,(a+b')}{a+a'+b+b'}-\frac{bb'-aa'}{a+a'+b+b'}\,e^{-(a+a'+b+b')\,\alpha t},\end{aligned}$$

and the quantity of AB present when equilibrium is established is

$$(a+b)\,(a+b')\,/\,(a+a'+b+b').$$

In the case in which AB, CD are present initially in equivalent quantities, each equal to $a$, and neither AC nor BD are initially present,

$$x=a\left\{1-m\,\frac{e^{\nu t}-1}{ne^{\nu t}+1}\right\}.$$

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Where $m = \alpha^{\frac{1}{2}}/(\beta^{\frac{1}{2}} - \alpha^{\frac{1}{2}})$, $n = (\beta^{\frac{1}{2}} + \alpha^{\frac{1}{2}})/(\beta^{\frac{1}{2}} - \alpha^{\frac{1}{2}})$, and when equilibrium is established the amount of AB or CD present is $a\beta^{\frac{1}{2}}/(\beta^{\frac{1}{2}} + \alpha^{\frac{1}{2}})$, and the amount of AC or BD present is $a\alpha^{\frac{1}{2}}/(\beta^{\frac{1}{2}} + \alpha^{\frac{1}{2}})$.

In the case in which there are originally present $a$ units of AB, $ra$ units of CD, and, at any subsequent time $t$, $a - y$ units of AB, $ra - y$ units of CD, and $y$ units of AC or BD,

$$\begin{aligned} \dot{y} &= \alpha\,(a - y)\,(ra - y) - \beta y^2 \\ &= (\beta - \alpha)\,(p - y)\,(q + y), \end{aligned}$$

$p$ and $-q$ being the roots of

$$(\beta - \alpha)\,y^2 + a\alpha\,(r + 1)\,y - \alpha ra = 0,$$

the course of the change is given by the equation

$$\log\,\{p\,(q + y)\,/\,q\,(p - y)\} = (\beta - \alpha)\,(p + q)\,t$$

or

$$y = pq\,(e^{\nu t} - 1)\,/\,(p + qe^{\nu t})$$

where $\nu = (\beta - \alpha)\,(p + q)$, and the equilibrium is established, theoretically after an infinite time, when there are present $a - p$ units of AB, $ra - p$ units of CD, and $p$ units of AC or BD.

The equations obtained in this case are applicable to the experiments contained in a paper by Dr. GLADSTONE published in the Transactions of the Royal Society ('Phil. Trans.,' vol. 145, p. 187). The most probable value of $a$ is 792, and of $(\beta - \alpha)/a\alpha$ is ·0705. Therefore $\beta = 57\alpha$, so that the rate of the change

$$\text{AC} + \text{BD} = \text{AB} + \text{CD}$$

is fifty-seven times the rate of the change

$$\text{AB} + \text{CD} = \text{AC} + \text{BD}.$$

The equation of the course of the change when $r = 1$ is

$$\log\left\{\cdot 766\left(\frac{\cdot 153 + y}{\cdot 117 - y}\right)\right\} = 15{\cdot}1\alpha t\,;$$

when $r = 15{\cdot}4$ it is

$$\log\left\{\cdot 576\left(\frac{\cdot 691 + y}{\cdot 398 - y}\right)\right\} = 60{\cdot}9\alpha t\,;$$

when $r = 125$ it is

$$\log\left\{\cdot 249\left(\frac{2{\cdot}99 + y}{\cdot 745 - y}\right)\right\} = 209\alpha t$$

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If in each of these cases the change is allowed to proceed until the value of $y$ is within 1 per cent. of the value $p$ which it attains, after a theoretically infinite time, when equilibrium is established, and $t_1$, $t_2$, $t_3$ are in each case the intervals from the commencement of the change to the instant when $y$ has the value $\cdot 99p$, then $t_1 : t_2 : t_3 = 30 : 7 : 2$ nearly; so that if the change reaches this point in the third case in two minutes, it will not reach it in the first case until the change has proceeded for at least half an hour. This fact probably accounts for the difference between the observed and calculated values of $y$ in the earlier part of the following table; for it is possible that the observations in the experiments in which a small quantity of potassium sulphocyanide was taken, were made before the change had practically reached its limit, in which case the observed values of $p$ would be too small. In the following table $r$ is the number of units of potassium sulphocyanide (the amount of ferric nitrate being unity), $p'$ the amount of red salt formed expressed in the arbitrary units adopted by Dr. GLADSTONE and $p$ the number of units of change when equilibrium is established.

| $r$. | $p$. | $p'$. | |
|---|---|---|---|
| | Calculated. | Found. | Calculated. |
| 1·0 | ·117 | 88 | 93 |
| 2·0 | ·164 | 127 | 130 |
| 3·2 | ·205 | 156 | 162 |
| 4·2 | ·231 | 176 | 183 |
| 5·4 | ·259 | 195 | 205 |
| 6·4 | ·279 | 213 | 221 |
| 9·4 | ·327 | 266 | 259 |
| 15·4 | ·398 | 318 | 316 |
| 21·0 | ·447 | 356 | 354 |
| 33·0 | ·522 | 419 | 414 |
| 45·0 | ·575 | 457 | 456 |
| 63·0 | ·634 | 508 | 502 |
| 81·0 | ·676 | 539 | 536 |
| 99·0 | ·710 | 560 | 562 |
| 125·0 | ·745 | 587 | 590 |

The relation between $p$ and $r$ is

$$(1 - p)(r - p) = 57p^2$$

and

$$p' = 792p.$$

From $r = 15 \cdot 4$ to $r = 125$ the calculated results agree with those found within the limits of experimental error, and the divergence of the earlier results in the table has been explained above.

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Another set of observations, p. 199 of the same paper, gives $a = 126$ $(\alpha - \beta) / a\alpha = \cdot 00596$, therefore $\alpha = 4 \cdot 07 \beta$. In this case the rate of the change

$$AB + CD = AC + BD$$

is nearly four times the rate of the reverse change

$$AC + BD = AB + CD.$$

In the following table $r$ is the number of units of potassium ferrocyanide (the amount of ferric citrate being unity), $p$ the number of units of change when equilibrium is established, $p'$ the amount of blue salt formed, in the arbitrary unit of Dr. Gladstone's paper.

| $r$. | $p$. | $p'$. | |
|---|---|---|---|
| | Calculated. | Found. | Calculated. |
| 1 | ·668 | 88 | 85 |
| 2 | ·847 | 107 | 107 |
| 3 | ·906 | 113 | 115 |
| 5 | ·942 | 120 | 119 |

The relation between $p$ and $r$ is

$$(1 - p)(r - p) = \cdot 246 p^2$$

and

$$p' = 126 p.$$

The experiments on p. 193 of the same paper are given in the following table. The ratio of the equivalents of ferric chloride and gallic acid is 1 : 1·26.

| $r$. | $p$. | $p'$. | |
|---|---|---|---|
| | Calculated. | Found. | Calculated. |
| 1·26 | ·624 | 88 | 89 |
| 2·52 | ·781 | 108 | 111 |
| 3·78 | ·845 | 120 | 120 |
| 5·04 | ·880 | 128 | 125 |
| 7·56 | ·919 | 133 | 131 |

The relation between $p$ and $r$ is

$$(1 - p)(r - p) = \cdot 63 p^2$$

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and

$$p' = 143p.$$

The experiments on p. 189, treated in the same way, give the relation

$$(1 - p)(r - p) = 95p^2.$$

In all these cases there occur a direct action and a reverse action, between which equilibrium is ultimately established. The ratio of the rates of the two actions is very different in the four cases here discussed; they are, taken in order, 57 : 1, 1 : 4, 1 : 1·6, 95 : 1. The cases chosen for calculation are those in which the curves representing the observations appear to be regular. The theoretical curve is in each case a hyperbola whose equation is of the form $(1 - y)(x - y) = my^2$.

A case of equilibrium similar to the cases here discussed has been investigated by one of us in a note appended to a paper by Professor DIXON, published in the Transactions of the Royal Society (' Phil. Trans.,' vol. 175, Part II., p. 682). The reactions considered in the note are

$$H^2O + CO = H^2 + CO^2,$$
$$H^2 + CO^2 = H^2O + CO.$$

If $\alpha$, $\beta$ are the rates of these reactions, the ratio $\beta : \alpha$ is shown to be independent of the quantities of the substances taking part in the reaction, and to depend upon the conditions of temperature, pressure, &c. The ratio $\beta : \alpha$ varies in the experiments made under different conditions from 2·7 to 7.

## ADDENDUM.

Received May 17, 1895.

Another kind of chemical equilibrium occurs when a substance C, which is formed by the reaction between the substances A and B, reacts with A to form B. After a time, which is theoretically infinite, the quantities of B and C remain constant, whilst the quantity of A is continually diminishing. The equations of these reactions are

$$A + B = C + D, \quad A + C = B + E.$$

Let $a$, $b$ be the masses of A, B, respectively, initially present, $x$, $y$, $z$ the masses of A, B, C present at a subsequent time $t$, then

$$\dot{x} = -(\alpha y + \beta z)\, x,$$
$$\dot{z} = (\alpha y - \beta z)\, x,$$

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$\alpha$ being the amount of each of A and B which react in an unit of time when an unit of each of them is present, and $\beta$ the amount of each of A and C which react in an unit of time when an unit of each of them is present. When the masses of B and C become constant, $\dot{z} = 0$ and $\alpha y = \beta z$, so that when equilibrium is established the mass of B is $b\beta/(\alpha + \beta)$, and the mass of C is $b\alpha/(\alpha + \beta)$. The quantity of A remaining afterwards is determined from the equation

$$\dot{x} = - 2\alpha\beta b x/(\alpha + \beta),$$

or

$$x = a_1 \text{ exp. } \{- 2\alpha\beta b t/(\alpha + \beta)\},$$

$a_1$ being the mass of A present when equilibrium is established, and $t$ the subsequent time.

The course of the chemical change previous to the establishment of equilibrium is sufficiently indicated by a study of the case when $\beta = \alpha$. The equations of the change become in this case

$$\dot{x} = - \alpha (y + z) x = - \alpha b x,$$
$$\dot{z} = \alpha (y - z) x = \alpha (b - 2z) x,$$

or

$$x = a \text{ exp. } (- \alpha b t),$$
$$\log \{b/(b - 2z)\} = 2a \{1 - \text{exp. } (- \alpha b t)\}/b.$$

It is seen from these equations that, after an infinite time, A is completely decomposed and the amounts of B and C present are $\frac{1}{2} b \{1 + \text{exp. } (- 2a/b)\}$ and $\frac{1}{2} b \{1 - \text{exp. } (- 2a/b)\}$, respectively. Theoretically, equilibrium between B and C has not been completely established unless $a$ is infinitely great in comparison with $b$.

An examination of a particular case will show that equilibrium may be very nearly established in a finite time. When $a = 5$, $b = 2$, $\alpha = ·25$, the following table of values are obtained:—

| $t$. | $x$. | $y$. | $z$. |
|---|---|---|---|
| ·5 | 3·89 | 1·33 | ·67 |
| 1 | 3·03 | 1·14 | ·86 |
| 2 | 1·84 | 1·04 | ·96 |
| 3 | 1·11 | 1·02 | ·98 |
| 4 | 0·68 | 1·01 | ·99 |
| 5 | 0·41 | 1·01 | ·99 |

This table shows that, within the usual limit of error in chemical experiments, equilibrium is practically attained after the reaction has proceeded for four minutes,

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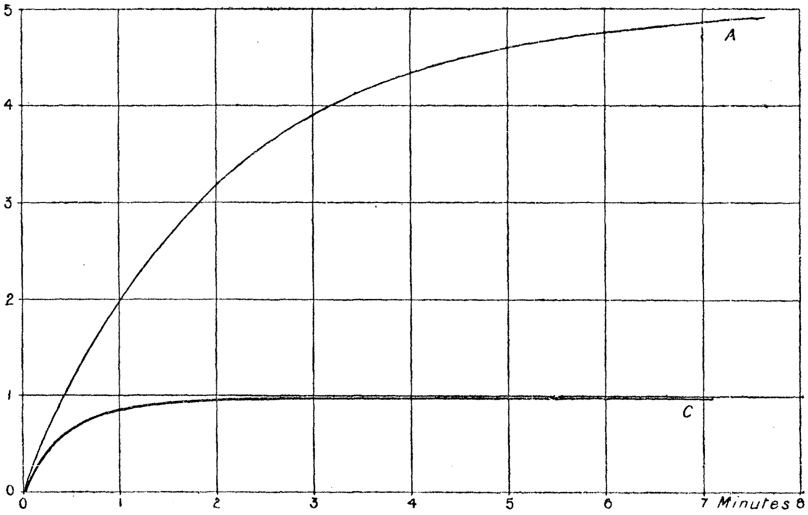
if the rate of change is such that when an unit mass of each of the substances undergoing change is present, one quarter of the total change is effected in one minute.

These results are represented graphically in the accompanying plate, in which the curves A and C represent the course of the change of the substances A and C.

This theory explains the case of equilibrium recorded on p. 854, in which the reactions are

$$H^2O^2 + 2HI = I^2 + 2H^2O,$$
$$H^2O^2 + I^2 = 2HI + O^2.$$

Diagram 6.



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