XLII.—*Reduction of Bromic Acid and the Law of Mass Action.*

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WITHIN the last few years the velocities of a large number of chemical reactions have been studied with the purpose of determining the mechanism of their transformations. Many of these have confirmed the theory connecting the velocity of a reaction with the number of molecules participating in it, whilst others have brought some new and remarkable facts to light. The great majority of them, however, only involve a reaction between at most two molecules, and very few of a more complex nature are known in which some subsidiary reaction does not complicate matters to such a degree that they cannot be made to yield simple mathematical results. The reduction of the oxygen acids of the halogens by hydriodic acid is a striking example of this class, and, although it has been studied by numerous chemists, it is only recently that it has been satisfactorily explained by Noyes (*Zeit. physikal. Chem.*, 1896, 19, 599). This is the more remarkable, as we should at first sight consider it to be of a quite simple nature. The experience of all those who have investigated it, however, has led to the opposite conclusion, and although Noyes has shown from Magnanini's determinations that the reaction between hydriodic and bromic acids is one of the *fourth* order, still nothing approaching to an absolute 'velocity constant' has been obtained.

The first reaction of this kind investigated was the interaction of bromic and hydriodic acids by Ostwald (*Zeit. physikal. Chem.*, 1888, 2, 127). He found that the values of k obtained from the equation $k = \frac{1}{t} \frac{x}{A(A-x)}$, instead of being constant, showed a continual decrease with the progress of the reaction, but he did not attempt to find a solution of the anomaly, as his object then was to determine the accelerating influence of different acids on the velocity of the reaction. The accelerating effect of the different acids employed was, in general, proportional to their affinity constants as determined by conductivity; but there were one or two exceptions, and notable among these was hydrobromic acid, which increased the velocity 10 per cent. more than the value of its affinity constant would have led him to expect. This fact suggests one disturbing influence in the action of hydriodic acid on bromic acid, because, according to the equation $6\text{HI} + \text{HBrO}_3 = \text{HBr} + 3\text{H}_2\text{O} + 3\text{I}_2$, hydrobromic acid is formed by the reaction. The

subject was next taken up by Meyerhoffer (*Zeit. physikal. Chem.*, 1888, 2, 585), who attempted to give expression to the other disturbing influence, namely, the retarding action of the liberated iodine. The existence of this retarding effect is much more apparent from the values obtained by another chemist who investigated the subject, namely, Burchard (*Zeit. physikal. Chem.*, 1888, 2, 796). He determined, not only the velocity of the reaction between bromic acid and hydriodic acid, but also employed iodic and chloric acids instead of bromic, and performed his experiments at a large number of different concentrations. The following tables, in which the original concentration of the one is double that of the other, contain some of the results of two of his experiments on HI and HIO_3 .

C=1.		C=2.	
<i>t</i> in minutes.	Iodine liberated.	<i>t</i> in minutes.	Iodine liberated.
5	3·3 milligrams.	10	38·25 milligrams.
10	5·4 „	15	40·88 „
20	8·82 „	20	42·11 „
30	11·13 „	30	43·99 „
∞	37·96 „	∞	75·92 „

In the second table it is evident that after 10 minutes the concentrations of the two acids are almost identical with their original concentrations in the first table. If the products of the reaction were without influence on its velocity, therefore, from this point onwards the amount of iodine liberated in a given time ought to be identical with that liberated in Table I; this is evidently not the case. From the middle point in Table II, there is liberated in 5 minutes only 2·63 milligrams of iodine instead of 3·3; in 10 minutes, 3·86 mg. instead of 5·4; and in 20 minutes, 5·74 mg. instead of 11·13. A like result, but more accurate, is got by using the interpolated values obtained from the curves. We mention this method here because it shows the magnitude of the retarding effect, and we shall make use of it afterwards to show that, in the action of bromic on hydrobromic acid, there is no such disturbing influence. Ostwald (*loc. cit.*) arrived at the same conclusion by adding a definite amount of iodine at the commencement. It is evident, therefore, that the action of hydriodic acid on the oxygen acids of the halogens is of too intricate a nature to give any satisfactory numerical results. For this reason, we have selected the reaction between bromic and hydrobromic acids for the subject of a special investigation.

Our first experiments were performed in presence of a large known excess of sulphuric acid, and the method we first employed for determining the amount of bromine liberated after a given time was in

principle the same as that used by Harcourt and Esson (Trans., 1867, 20, 476) in their investigation of the action of hydriodic acid on hydrogen peroxide. Measured volumes of one-fifth normal solutions of potassium bromide and potassium bromate were added to a definite volume of water and, after the addition of 1 c.c. of a decinormal solution of sodium thiosulphate, the beaker containing the solution was placed against a white background and stirred vigorously while 25 c.c. of a 12-times normal solution of sulphuric acid was rapidly run in. The amount of water taken was so adjusted that the volume of the whole was 500 c.c. In one case where the volume was 250 c.c., only 12.5 c.c. of the sulphuric acid solution were added, so that the concentration of the sulphuric acid was practically the same. The oxidation of the thiosulphate by bromine takes place according to the equation $4\text{Br}_2 + \text{Na}_2\text{S}_2\text{O}_3 + 4\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 + 8\text{HBr}$, and the point of complete oxidation of the thiosulphate was made evident by the appearance of the yellow colour of bromine in the solution, the time was then noted, and 1 c.c. more thiosulphate added. With the concentrations given above, 5 c.c. of potassium bromate solution is in every case equivalent to 7.5 c.c. of the thiosulphate solution; it was therefore possible to obtain 7 readings for 5 c.c. of potassium bromate, 22 with 15 c.c., &c. This method of estimating the amount of bromine is interesting for this reason that, whilst the concentration of bromic acid continually decreases from the reaction $5\text{HBr} + \text{HBrO}_3 = 3\text{H}_2\text{O} + 3\text{Br}_2$, that of the hydrobromic acid continually increases, because the 6 atoms of bromine are at once reconverted into hydrobromic acid; the form of the equation connecting the velocity with the concentration must therefore be modified to express this. Taking A and $5A$ as the original concentrations of bromic and hydrobromic acid respectively, when 5 c.c. of 0.2 normal bromic, and 25 c.c. of 0.2 normal hydrobromic acids are contained in 500 c.c., after x grams of bromic acid have disappeared, its concentration will be $A - x$, whilst that of the hydrobromic acid will be $5A + x$, and the expression for the velocity is $dx/dt = k(5A + x)(A - x)$. Under the conditions of the experiment, a very small quantity of hydrobromic acid is therefore capable of transforming an unlimited amount of bromic acid; this circumstance was made use of to obtain a larger number of readings by varying the amount of bromic acid added. A larger amount of bromic acid required, of course, the addition of a proportionately larger quantity of thiosulphate solution, and on this account the error introduced by using 20 c.c. of bromic acid or 30 c.c. of thiosulphate solution is by no means negligible towards the end, although it is practically so during the first third of the reaction. The experiments requiring more thiosulphate were, however, performed to examine the

influence of the thiosulphate itself on the velocity of the reaction. In order to reduce the labour of calculation and to make all our computed values comparable, we have taken the original concentration $A = 7.5$, that is, the number of c.c. of decinormal thiosulphate required for 5 c.c. of 0.2 normal bromic acid. The amount of thiosulphate required at any time, t , therefore represents x , the quantity of bromic acid which has been reduced up to that time. When varying amounts of hydrobromic acid are added to this same amount of bromic acid, the general equation connecting concentration with velocity is $dx/dt = k(nA + x)(A - x)$, which gives on integration

$$k = \frac{1}{(n+1)At} \log_e \frac{nA+x}{n(A-x)}$$

as the value of k , the velocity constant, or, substituting ordinary for natural logarithms, $k = \frac{1}{0.4343(n+1)At} \log \frac{nA+x}{n(A-x)}$.

The following tables, I. to V., contain the results of a series of experiments made at 20° with an increasing amount of hydrobromic acid. The concentration in Table VI. is half that in Table III., and in Table VII. is double of that in Table I. Each value of t , the time, is the mean of a number of observations. x = c.c. of thiosulphate, t in minutes.

TABLE I.

$v = 500$ c.c., 5 c.c. KBr and 5 c.c. KBrO_3 .

x	t	k
1	1.34	0.0133
2	3.0	0.0121
3	4.84	0.0117
4	7.0	0.0113
5	9.65	0.0111
6	13.3	0.0110
7	19.6	0.0115

TABLE II.

$v = 500$ c.c., 10 c.c. KBr and 5 c.c. KBrO_3 .

x	t	k
1	0.8	0.0115
2	1.77	0.0109
3	2.85	0.0108
4	4.22	0.0105
5	5.87	0.0105
6	8.32	0.0104
7	12.38	0.0111

TABLE III.

$v = 500$ c.c., 15 c.c. KBr and 5 c.c. KBrO_3 .

x	t	k
1	0.68	0.0089
2	1.49	0.0088
3	2.46	0.0086
4	3.6	0.0086
5	5.09	0.0085
6	7.18	0.0086
7	11.1	0.0089

TABLE IV.

$v = 500$ c.c., 20 c.c. KBr and 5 c.c. KBrO_3 .

x	t	k
1	0.6	0.0078
2	1.33	0.0073
3	2.15	0.0075
4	3.15	0.0075
5	4.48	0.0074
6	6.39	0.0074
7	10.23	0.0076

TABLE V.

 $v=500$ c. c., 25 c. c. KBr and 5 c. c. KBrO_3 .

x	t	k
1	0.48	0.0078
2	1.1	0.0073
3	1.81	0.0072
4	2.67	0.0072
5	3.81	0.0071
6	5.45	0.0072
7	8.68	0.0074

TABLE VI.

 $v=1000$ c. c., 15 c. c. KBr and 5 c. c. KBrO_3 .

x	t	k
1	1.5	0.0083
2	3.15	0.0084
3	5.0	0.0085
4	7.4	0.0083
5	10.5	0.0082
6	14.2	0.0087
7	23.4	0.0085

TABLE VII.

 $v=250$ c. c., 5 c. c. KBr and 5 c. c. KBrO_3 .

x	t	k	x	t	k
1	0.79	0.0113	5	5.76	0.0093
2	1.82	0.0100	6	7.79	0.0094
3	2.93	0.0096	7	11.33	0.0099
4	4.22	0.0094			

A comparison of these results shows that, from Tables I. and VII. alone, in which the substances are present in the same relative proportions, we might be led to conclude that the reaction is a pure one of the second order, since the value of k does not vary very greatly from a mean of 0.0100. The same is even more strictly true of Tables III. and VI., where it only varies from 0.0089 to 0.0082. When, however, the values obtained from the other concentrations are also taken into account, it becomes at once evident that the reaction can by no means be looked upon as a simple one and free from disturbing influences, for the value of k falls continuously with an increasing amount of hydrobromic acid, or, in other words, increases with an increasing amount of bromic acid. This is also apparent from the two following series, where a larger amount of bromic acid was employed with the same amount of hydrobromic acid as in Table I. The equation connecting velocity and concentration is in this case slightly different, that is, $dx/dt = k(A+x)(nA-x)$ where $A+x$ is the concentration of the hydrobromic acid after any interval. This equation, when integrated,

gives $k = \frac{1}{(n+1)At} \log_e \frac{n(A+x)}{nA-x}$ or, employing ordinary logarithms,
 $k = \frac{1}{0.4343(n+1) \times At} \log \frac{n(A+x)}{nA-x}.$

TABLE VIII.

 $v = 500$ c.c., 5 c.c. KBr and 10 c.c. KBrO_3 .

x	t	k
1	0.68	0.0126
2	1.53	0.0110
3	2.33	0.0107
4	3.15	0.0104
5	4.05	0.0103
6	4.92	0.0099
7	5.83	0.0098
8	6.82	0.0097
9	7.9	0.0096
10	9.1	0.0095

TABLE IX.

 $v = 500$ c.c., 5 c.c. KBr and 15 c.c. KBrO_3 .

x	t	k
1	0.43	0.0131
2	0.96	0.0113
3	1.49	0.0107
4	2.00	0.0104
5	2.52	0.0101
6	3.00	0.0100
7	3.52	0.0098
8	4.02	0.0097
9	4.54	0.0095
10	5.07	0.0094

In these, the value of k does not vary about a mean but decreases continually, so that the mathematical expressions above cannot be regarded as accurate representations of the reaction.

As no other equation of a higher order could be found to give better results, and as the agreement already referred to in series I. and VII., and in III. and VI., where all the reacting substances, namely, bromic acid, hydrobromic acid, and sodium thiosulphate, are present in the same proportions, pointed to the reaction being one of the second order, we were driven to the conclusion that the thiosulphate must be the disturbing agent. In order to test this point, the following experiments were made. Each solution contains the same amount of potassium bromide and bromate, but the thiosulphate was added to them in quantities of 1 c.c., 5 c.c., 10 c.c., and 15 c.c. respectively. x = c.c. of thiosulphate; t in minutes.

TABLE X.

 $v = 500$ c.c.; 5 c.c. KBr and 20 c.c. KBrO_3 .

	1 c.c. at a time.	5 c.c.	10 c.c.	15 c.c.
x	t	t	t	t
5	2	1.13	—	—
10	3.82	2.57	1.9	—
15	5.68	4.05	—	3
20	7.83	5.48	4.97	—

From this table, it would appear that probably as much of the thiosulphate is directly oxidised by the bromic acid as by the liberated bromine. This reaction between bromic acid and thiosulphate was further proved by adding a drop of the latter to a solution of bromic acid which contained no hydrobromic acid, when bromine was almost instantly liberated. The remarkable observation was made, on carrying the four series included in Table X to completion, that the total time required for the reduction of the whole of the bromic acid present was the same in each case. This is, so far as we are aware, the first

instance which has been observed of a reaction proceeding by two distinct paths to the same end point in the same time, and is doubtless a necessary consequence of the relative changes in concentration of the three reagents under these particular experimental conditions.

After the method described above had been shown to be useless for the object which we had in view, there only remained the more tedious and somewhat less accurate one of titrating the liberated bromine with sodium thiosulphate. In employing this method, it was of course necessary to make up a fresh solution for each reading, as the employment of pipettes would have caused a considerable loss of bromine vapour. We therefore selected a number of 250 c.c. flasks with long necks and well-ground stoppers, introduced into them the potassium bromide, potassium bromate, and sulphuric acid solutions together with the water necessary to make the volume up to 100 c.c., placed them in a thermostat at 20°, and after a definite interval titrated the liberated bromine rapidly with N/100 thiosulphate solution. The 5 c.c. of 12-times normal sulphuric acid solution was, of course, introduced last in order to start the reaction, and the time noted from its addition. The following tables contain the mean results of a large number of experiments performed in the manner described; c.c. of thiosulphate N/100 *t* in minutes.

TABLE XI.

v = 100 c.c., 5 c.c. KBr and 1 c.c. KBrO₃.

c.c. of thiosulphate.	<i>t</i> .	<i>k</i> .
2.3	1	0.00483
3.6	2	0.00421
4.9	3	0.00431
5.8	4	0.00421
6.6	5	0.00419
7.25	6	0.00415
7.75	7	0.00406
8.35	8	0.00419
8.8	9	0.00407
11.3	20	0.00407

TABLE XII.

v = 100 c.c., 10 c.c. KBr and 1 c.c. KBrO₃.

c.c. of thiosulphate.	<i>t</i> .	<i>k</i> .
4.2	1	0.00474
6.6	2	0.00442
8.35	3	0.00433
9.8	4	0.00443
10.75	5	0.00436
11.6	6	0.00442
12.3	7	0.00452
12.8	8	0.00483

TABLE XIII.

v = 100 c.c., 10 c.c. KBr and 2 c.c. KBrO₃.

c.c. of thiosulphate.	<i>t</i> .	<i>k</i> .	c.c. of thiosulphate.	<i>t</i> .	<i>k</i> .
8.1	1	0.00493	18.0	5	0.00400
13.0	2	0.00510	19.4	6	0.00407
14.8	3	0.00433	20.8	7	0.00431
16.5	4	0.00407	21.7	8	0.00436

In order to make these tables comparable with the former series, the observed readings must be multiplied by 5, since only 100 c.c. are employed, and divided by 10, because N/100 thiosulphate is used for titration instead of decinormal. If A is taken equal to 7.5 as before, the observed readings must, therefore, be divided by 2, and the equations to be employed are

$$\text{For XI.} \quad k = \frac{1}{5t} \cdot \frac{x}{A(A-x)},$$

$$\text{For XII.} \quad k = \frac{1}{0.4343 \times 5 \times t} \log \frac{2A-x}{2(A-x)},$$

$$\text{And for XIII.} \quad k = \frac{1}{10t} \cdot \frac{x}{A(2A-x)}.$$

These are all equations of the second order, and an examination of the values of k shows an agreement which is remarkable, considering the comparative crudeness of the experimental method. It is also a much lower number than that obtained by the previous experimental method, showing the great influence of the thiosulphate on the velocity of reaction. In strong sulphuric acid solution, the reaction between bromic and hydrobromic acids is, therefore, without doubt a reaction of the second order. The question as to how this is possible is best answered, as Noyes has pointed out, by assuming that the reaction takes place in different stages, some of which are infinitely quick compared with the others. For example, we may assume that the first stage consists in the formation of bromous and hypobromous acids, which are then at once decomposed by the hydrobromic acid, thus.

If this were so, we should expect to find in the light of the ionic theory that the reaction, which in the presence of a large excess of sulphuric acid is bimolecular, in its absence is of a higher order, probably quadrimolecular, because not only do the Br and BrO₃ ions decrease in number, but the hydrogen ions also decrease from the formation of the two weak acids HBrO₂ and HBrO. This expectation was completely fulfilled by an examination of the reaction velocity between hydrobromic and bromic acids in the absence of sulphuric or any other strong acid.

A pure, normal hydrobromic acid solution was prepared by distilling ordinary hydrobromic acid, and diluting it to the requisite volume, and a solution of pure bromic acid was made by digesting pure barium bromate with dilute sulphuric acid at a low temperature until neither sulphuric acid nor barium chloride gave any precipitate. The strength of the solution was determined by adding excess of standard soda solution and titrating the excess with standard hydrochloric acid, using

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litmus as indicator; it was then made up exactly to N/5. In performing the experiments on the velocity of the reaction, water and the mixture of the acids were used in volume sufficient to give 100 c.c. or 150 c.c., and the free bromine was estimated by an approximately N/100 thiosulphate solution. The time was noted from the addition of the hydrobromic acid, which was introduced from a fast-running pipette; the experiments were carried out at a temperature of 25°. It was found by special experiments, in which an excess of sulphuric acid was added, that the total amount of bromine was equivalent to 77 c.c. of thiosulphate solution. This value represents A in the equations given below, and x is the observed amount of thiosulphate required in any particular observation.

TABLE XIV.

$v=100$ c.c., 5 c.c. HBr and 5 c.c. HBrO_3 .

c.c. of thiosulphate. t .			c.c. of thiosulphate. t .		
		k .			k .
6.8	2	0.000000117	25.1	15	0.000000110
11.6	4	0.000000115	28.7	20	0.000000111
15.1	6	0.000000111	34.0	30	0.000000115
18.1	8	0.000000112	37.7	40	0.000000119
20.25	10	0.000000109	41.8	60	0.000000115
23.75	13	0.000000114			

TABLE XV.

$v=150$ cc., 5 c.c. HBr and 5 c.c. HBrO_3 .

c.c. of thiosulphate.	x .	t .	k .
5.05	3.37	4	0.000000139
8.20	5.47	8	0.000000124
10.8	7.2	12	0.000000118
15.5	10.33	20	0.000000119
19.9	13.27	30	0.000000119
27.65	18.44	60	0.000000115
36.0	24.0	120	0.000000116

In Table XV., the concentration is only two-thirds of that in XIV., so that A must be taken as 51.33, and x as two-thirds of the observed reading. It was, of course, necessary to determine whether the reaction proceeds to an end in the absence of sulphuric acid, or if there is an equilibrium point due to the action of the liberated bromine on the water, such as is generally supposed to take place. For this purpose, we introduced the reagents in the proportions and quantities given above into flasks which were at once sealed, and allowed to stand for several days at 25° before titration. The results show that most of the bromic acid is reduced, but they do not exclude the formation of

hypobromous acid, which may possibly be readily titrated by thio-sulphate.

$v=100$ c.c., 5 c.c. HBr and 5 c.c. HBrO_3 .

c.c. of thiosulphate. t in days.

70	7
71	11
72.5	20

$v=150$ cc., 5 c.c. HBr and 5 c.c. HBrO_3 .

c.c. of thiosulphate. t in days.

67	9
69.8	18

An investigation of the curves of these two velocities, however, makes it clear that the backward reaction of bromine on water must be so slight as to be negligible. When one-third of the stronger solution is decomposed, it evidently has the same concentration as the more dilute does at the commencement, except that there is bromine present. If from this point onwards, therefore, there is the same amount of bromine liberated in the same time, the bromine can have no disturbing influence whatever. This point, namely, 25.7, is found from the curve to be reached in 16 minutes, and the values to be tested are therefore

c.c. thiosulphate.	t in minutes.
3.0	4
8.3	14
12.0	24
16.1	44

These points are indicated by a circle upon the curve, and the curve passing through them is found to coincide exactly with that representing the values in Table XV.

After having shown that there is no equilibrium point, the determination of the order of the reaction is quite simple. The method is

described fully in *Studien zur Chemischen Dynamik*, by Cohen, page 106. Two solutions are taken containing the reagents in equivalent quantities as above, but of different concentration, c_1 and c_2 , and the times, t_1 and t_2 , necessary for the transformation of the same fraction of both are determined, by substituting these values in the equation

$$n = 1 + \log \frac{t_1}{t_2} / \log \frac{c_2}{c_1}$$

the value of n in the equation $dc/dt = kc^n$ is obtained.

By interpolation, it is found from the curves that the time necessary for the decomposition of one-third of the solution whose concentration is 77 is 15 minutes, whilst the solution of concentration 51.33 requires 50 minutes. Substituting these experimental values, we find $n = 1 + \log 3.333 / \log 1.5 = 1 + 2.97 = 3.97$.

This is as close an approximation to 4 as could be desired, and the reaction must, therefore, be one of the fourth order. In order to calculate the value of the velocity constant, since the substances are present in equivalent, not molecular, quantities, and since an equivalent of each disappears simultaneously, we may call A the initial concentration of both bromic and hydrobromic acid, and the equation connecting velocity with concentration is $dx/dt = k(A - x)^4$, which gives, on integration,

$$k = \frac{1}{3t} \left[\frac{1}{(A - x)^3} - \frac{1}{A^3} \right]$$

The values obtained for k by means of this equation in tables XIV. and XV. are quite satisfactory; there can, therefore, be no doubt that when the pure acids are allowed to act on each other, the reaction is one of the fourth order.

Conclusion.

As has been already mentioned, Noyes (*loc. cit.*) has pointed out the mechanism when hydriodic acid is the reducing agent, and a similar one must hold in the case of hydrobromic acid. Since that stage of the reaction, which requires a measurable time for its completion, is one of the fourth order, four individuals must take part in it, or, according to van't Hoff's thermodynamic deductions, four 'osmotic units' must be simultaneously transformed. This is clearly expressed

by the ionic equation $2\overset{+}{\text{H}} + \text{Br} + \text{Br}\overset{-}{\text{O}}_3 = \text{HBrO} + \text{HBrO}_2$ where the four individuals, two hydrogen, one bromine, and one bromate ion, are converted into the substances hypobromous and bromous acids which, like the weak acids, hypochlorous, boric, and carbonic, are very lightly ionised. This conclusion is supported by the result obtained in presence of a large excess of sulphuric acid. There the number of hydrogen ions is so large that they relatively undergo no change of

concentration. This is expressed by the equation $\propto \overset{+}{\text{H}} + \overset{-}{\text{Br}} + \overset{-}{\text{BrO}_3}$
 $= \overset{+}{\text{H}} + \text{HBrO} + \text{HBrO}_2$ or $\overset{-}{\text{Br}} + \overset{-}{\text{BrO}_3} = \text{HBrO} + \text{HBrO}_2$, and in accordance with this we find that in presence of a large excess of sulphuric acid the reaction is bimolecular. The velocity when pure bromic and hydrobromic acids are used is therefore directly proportional to the concentrations of the bromate and bromine ions, and proportional to the square of the concentration of the hydrogen ions. This result has already been deduced by Noyes for the reduction of bromic acid by hydriodic acid, and therefore the gradual formation of hydrobromic acid in the latter reaction can exercise but little disturbing influence. We should expect, therefore, the reduction by hydrobromic acid to be much slower than by hydriodic acid. The following calculation shows that this is so. Ostwald found that in a solution which contained 0.2389 gram HBrO_3 per litre, 0.0846 gram was reduced in 81 minutes at 25° . Substituting these values for A , x , and t in the equation $k = \frac{1}{3t} \left[\frac{1}{(A-x)^3} - \frac{1}{A^3} \right]$, the value of k is found to be 0.818.

In the experiment with hydrobromic acid given in Table XIV., the original concentration of bromic acid is 1.29 grams per litre, and after 15 minutes 0.4205 gram has been reduced. This gives 0.023 as the value of k . This number is not, however, directly comparable with Ostwald's, because the solution only contains 5 molecules of HBr to 1 of HBrO_3 , whilst his contains 6 molecules of HI to 1 of HBrO_3 . It must therefore be multiplied by $5/6$, the ratio of the halogen ions, and also by $36/49$, the square of the ratio of the hydrogen ions. The result is that $k = 0.014$. Hence the reduction by hydriodic acid takes place $818/14 = 58.4$ times as fast as the reduction by hydrobromic acid, when they are present in equivalent quantities. The slow formation of the latter, therefore, in no way vitiates the conclusions drawn by Noyes from a study of the reaction between bromic and hydriodic acids.

This deduction receives confirmation from the values obtained by Ostwald (*loc. cit.*) in his investigation on the accelerating influence of different acids on the velocity of the reduction of bromic by hydriodic acid. He found that when no other acid was added, 164 minutes were required for the reduction of a definite amount of the bromic acid. 36.6 minutes only were required when a quantity of hydrochloric acid equivalent to the hydriodic acid was added, and 33.8 minutes when a similar quantity of hydrobromic acid was added. We have satisfied ourselves that hydrochloric acid, if it reduces bromic acid at all under the conditions he employed, does so extremely slowly; the whole acceleration which it produces is therefore due to the increase in number of the hydrogen ions. There is the same increase when

hydrobromic acid is added, due to the same cause, for the two are almost equally dissociated, but a further acceleration of 2·8 minutes due to the action of the bromine. Could the same amount of bromine ions, therefore, be added without hydrogen ions, the time required would be 161·2 minutes, therefore the velocity of the reduction by hydriodic acid is $164 \div (164 - 161\cdot2) = 58\cdot6$ times greater than by hydrobromic acid, a value in almost perfect agreement with that obtained by the former method.

In conclusion, we wish to express our thanks to Professor Ramsay, who proposed the research, and has given us much valuable advice during its progress.

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