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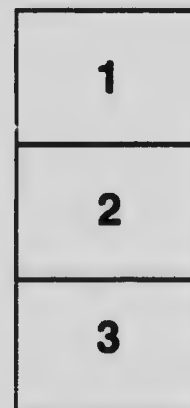
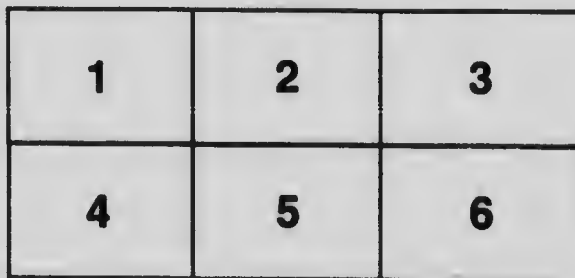
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No. 58: THE RATES OF THE REACTIONS IN SOLUTIONS  
CONTAINING POTASSIUM BROMATE, POTASSIUM IODIDE,  
AND HYDROCHLORIC ACID, BY ROBERT H. CLARK

(REPRINTED FROM THE JOURNAL OF PHYSICAL CHEMISTRY, VOL. X.)

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THE RATES OF THE REACTIONS IN SOLUTIONS CONTAINING POTASSIUM BROMATE, POTASSIUM IODIDE AND HYDROCHLORIC ACID

BY ROBERT H. CLARK

Among the earliest contributions to the literature of this subject is a paper by W. Ostwald,<sup>1</sup> who studied the reaction between hydrogen iodide and bromate in order to determine the accelerating influence of different acids. The author did not attempt to formulate a satisfactory kinetic equation, but calculated the velocity constant from the bi-molecular formula, and came to the conclusion that, in general, the accelerating influence of the different acids is proportional to their affinity constants,<sup>2</sup> the chief exception being in the case of chromic acid. I have carried out a number of experiments on the action of chromic acid, which will appear in a second communication.

In the same year W. Meyerhoffer<sup>3</sup> and O. Burchard,<sup>4</sup> working independently of each other, investigated the reaction and both came to the conclusion that the rate could not be represented by the formula of the second order or by any other simple formula. Meyerhoffer ascribed the complications to the influence of the iodine formed by the reaction and proposed the equation  $\frac{dx}{dt} = \frac{c(a-x)^2}{x}$ , but it was shown later by Meyer<sup>5</sup> that this equation is not in agreement with the experiments.

In 1890 Gactano Magnanini<sup>6</sup> made a great many measurements on the rate of this reaction; he, like Ostwald, studied the influence of different acids and noted that the acceleration caused by hydrochloric, nitric and sulphuric acids is not

<sup>1</sup> Zeit. phys. Chem., 2, 127 (1888).

<sup>2</sup> See however, Zeit. phys. Chem., 19, 599 (1891) and Table IV of the present paper, p. 684.

<sup>3</sup> Ibid., 2, 585 (1888).

<sup>4</sup> Ibid., 2, 796 (1888).

<sup>5</sup> Zeit. phys. Chem., 2, 830 (1888).

<sup>6</sup> Gazz. chim. Ital., 20, 377 (1890).

proportional to their concentrations, but failed to draw any general conclusions.

The next paper on the subject, A. A. Noyes<sup>1</sup> "Contribution to the Knowledge of the Order of Polymolecular Reactions," contains four series of experiments by W. O. Scott, in which the initial concentrations of potassium bromate and iodide were varied, while in all the acid was present in constant excess. Comparison of the constants of the second and third order in the different series led to the conclusion that "the reaction between hydriodic and bromic acids is of the second order."

In the following year in a paper "On the Catalytic Effect of Hydrion on Polymolecular Reactions"<sup>2</sup> Noyes showed from certain of Magnanini's measurements, that the rate of the reaction between hydrobromic and bromic acids is proportional to the square of the concentration of the hydrion.

In spite of this large amount of work, however, the author of the most recent text-book on chemical kinetics<sup>3</sup> is of the opinion that "the course of the oxidation of hydriodic acid by the oxyacids of the halogens appears to be so intricate that a satisfactory application of the mass law has not yet been made." The measurements of the present paper show definitely the influence of the concentration of each reagent on the rate, and the extent to which the results are affected by the presence of the products of oxidation, *viz.*, iodine and bromide.

#### Plan of the Experiments

In these measurements, in order to trace the effect of the concentrations of each one of the chemicals separately, I have adopted a plan described by Mr. W. C. Bray<sup>4</sup> under the title "Method of Constant Rates" which consists in choosing the concentrations so that "while the amount of change accomplished in a suitable interval of time is sufficient for the

<sup>1</sup> Zeit. phys. Chem., 18, 118 (1890).

<sup>2</sup> Ibid., 19, 599 (1891).

<sup>3</sup> J. W. Mellor: "Chemical Statics and Dynamics," p. 103 (1904).

<sup>4</sup> Jour. Phys. Chem., 7, 93 (1903).



requirements of an accurate analysis, yet the fractional alteration in the concentrations of the reagents involved is so small that the rate may be treated as practically constant during the interval." Where the reaction has proceeded so far that this assumption could not be made, a correction has been applied for the small changes in concentrations of the reagents involved. In all cases these corrections are comparatively small, the conclusions to be drawn from the experiments being, in general, obvious enough, even without the correction.

#### Method of Work

*Temperature.*—All the measurements were made at 30°, this temperature being maintained by a thermostat within one-tenth of a degree.

*Calibration.*—All the pipettes used were calibrated by weighing the distilled water discharged, thirty seconds being allowed for drainage. The burettes were calibrated as described in "Ostwald's Hand- und Hilfsbuch," p. 103.

*Details of an Experiment.*—Each measurement contained in the following tables involved the preparation of a new reacting mixture. Portions of the stock solutions used in the measurements were kept in the thermostat in glass-stoppered flasks. The potassium bromate was added to a suitable volume of water in a wide-mouthed half-liter glass-stoppered bottle, while the potassium iodide and hydrochloric acid were pipetted into a large test-tube together with enough water to make up a volume of 80 cc. After pipetting out the solutions they were allowed to stand in the thermostat for five minutes, and then the contents of the test-tube were quickly poured into the bottle and shaken, the exact time of mixing being noted. The total volume of the reacting mixture was always 250 cc. When it was desired to stop the reaction the contents of the bottle were rapidly stirred, 10 cc of a half-saturated ammonium bicarbonate solution were thrown in, and the time was noted. The iodine liberated was then determined with hundredth-normal arsenite.

**Stock Solutions**

*Potassium Bromate*.—0.0206 F.<sup>1</sup> made from Merck's potassium bromate and standardized by decomposing a known volume with excess of potassium iodide and hydrochloric acid, adding excess of the solution of ammonium bicarbonate, and titrating against the volumetric sodium arsenite.

*Potassium Iodide*.—0.9890 F. neutralized (to litmus) by hydriodic acid and standardized gravimetrically with silver.

*Potassium Bromide*.—2.002 F. neutralized and standardized with silver.

*Hydrochloric Acid*.—Two solutions 0.9539 F. and 0.9542 F. respectively, by comparison (phenolphthalein) with a freshly prepared volumetric potassium solution, which in turn was standardized with potassium bichromate.

*Sodium Arsenite*.—0.02504 F.  $\text{As}_2\text{O}_3$  (0.10017 normal) prepared according to Mohr<sup>2</sup> and standardized with dry freshly sublimed iodine.

*Iodine*.—Approximately decinormal, prepared from freshly sublimed iodine and compared frequently with the sodium arsenite, the accurate titre so found being used in the calculations.

*Ammonium Bicarbonate*.—A half-saturated solution was kept under carbon dioxide; it was tested from time to time, and not used unless a distinct blue color was obtained by adding one drop of centinormal iodine to a mixture of 250 cc water, 10 cc ammonium bicarbonate, 10 cc potassium iodide and 3 cc starch.

*The Starch* was prepared fresh daily: 1 gram to the liter.

All these solutions were diluted to one-tenth their concentration to form the "stock solutions" and volumetric solutions referred to in the preceding section.

**Explanation of the Tables**

The numbers at the head of each table, divided by 100,000, give the gram-formula weights of each reagent initially present

<sup>1</sup> Formula weights per liter.

<sup>2</sup> Chemisch-Anal. Titrimethode, 9th ed., p. 392.

in the 250 cc of reacting mixture. Under  $t$  is given the duration of the oxidation in minutes; under  $x$  the iodine liberated, expressed as cubic centimeters of 0.010017 normal arsenite solution; and under  $x'$  these values corrected for the falling off in concentration of the reagents.<sup>1</sup>  $R_0 = \frac{dx}{dt} (x=0)$  is the "initial rate," *i. e.*, the number of cubic centimeters of hundredth-normal iodine liberated per minute in the 250 cc of reacting mixture whose composition is, and remains, that given at the head of the table. Under  $K$  is given the "constant of the fourth order" multiplied by  $10^{13}$ .

The experiments of Table I are the standard with which are compared those of Tables II, III and IV where the concentrations of the bromate, iodide and acid respectively are doubled.

**Effect of Bromate, Iodide and Acid**

TABLE I

KBrO<sub>3</sub>, 20.5; KI, 98.67; HCl, 95.15

$t$	$x$	$x'$	$R_0 \times 10^4$	$K \times 10^{13}$
5	0.23	0.231	462	99
10	0.45	0.454	454	97
20	0.89	0.907	453	100
30	1.40	1.44	480	103
45	2.15	2.25	500	104
60	2.80	2.99	498	103
90	4.15	4.56	506	104

Average value,  $R_0 = 481 \times 10^{-4}$

TABLE II

KBrO<sub>3</sub>, 41; KI, 98.67; HCl, 95.15

$t$	$x$	$x'$	$R_0 \times 10^4$	$K \times 10^{13}$
5	0.46	0.464	928	99
10	0.90	0.907	907	97
20	1.80	1.87	935	100
30	2.75	2.90	966	103
45	4.00	4.32	960	104
60	5.24	5.79	965	103
90	7.60	8.77	973	104

Average value,  $R_0 = 948 \times 10^{-4}$

<sup>1</sup> See pages 681 and 685.

TABLE III  
 KBrO<sub>3</sub>, 20.5; KI, 197.3; HCl, 95.15

<i>t</i>	<i>x</i>	<i>x'</i>	R <sub>0</sub> × 10 <sup>4</sup>	K × 10 <sup>13</sup>
5	0.45	0.454	908	97
10	0.90	0.915	915	98
20	1.80	1.86	930	99
30	2.75	2.88	960	102
45	3.99	4.30	955	102
60	5.22	5.73	955	102
90	7.53	8.66	962	102

Average value, R<sub>0</sub> = 936 × 10<sup>-4</sup>

TABLE IV  
 KBrO<sub>3</sub>, 20.5; KI, 98.67; HCl, 190.3

<i>t</i>	<i>x</i>	<i>x'</i>	R <sub>0</sub> × 10 <sup>4</sup>	K × 10 <sup>13</sup>
5	0.92	0.934	1860	100
10	1.85	1.91	1910	102
20	3.62	3.74	1870	100
30	5.39	5.91	1970	105
45	7.75	8.87	1970	105
60	9.76	11.60	1930	102
90	13.93	18.01	2000	106

Average value, R<sub>0</sub> = 1930 × 10<sup>-4</sup>

### Effect of Chlorion and of Atmospheric Oxygen on the Rate

In order to assure myself that the effect of the hydrochloric acid was due entirely to the concentration of the hydrion I made some measurements in which the concentration of the chlorion was doubled by adding sodium chloride. The rate was the same as in the absence of the salt. The addition of very large quantities of potassium chloride, however, retards the oxidation, see Tables IX and X and p. 688.

To find whether the results were affected by access of air,<sup>1</sup> I made some preliminary measurements in duplicate, one of each pair under ordinary conditions, and the other in an atmosphere of carefully purified carbon dioxide.<sup>2</sup> I

<sup>1</sup> Compare *Zeit. phys. Chem.*, 2, 103 (1888), and *Gazz. chim. Ital.*, 20, 382 (1890).

<sup>2</sup> See Dushman: *Jour. Phys. Chem.*, 8 (1904).

failed to detect any difference in the rates in the two cases, and the subsequent measurements were carried out in air.

**Effect of the Concentrations of Bromate, Iodide and Acid on the Rate**

By comparing Table I with II, III and IV respectively it is readily seen that the velocity of the reaction is proportional to the first power of the concentrations of the bromate and iodide and to the second power of that of the acid, as represented by the equation:

$$\frac{1}{V} \cdot \frac{dx}{dt} = \frac{(A-x)}{V} \frac{(B-x)}{V} \frac{(C-x)^2}{V^2} \quad (1)$$

This conclusion is confirmed by the constancy of K in the tables as calculated from the integrated form of the above equation:—

$$\frac{KABC^2t}{V^3} = x' = x + \frac{1}{2} \left( \frac{1}{A} + \frac{1}{B} + \frac{2}{C} \right) x^2 + \frac{1}{3} \left( \frac{1}{A} + \frac{1}{B} + \frac{3}{C} + \frac{1}{AB} + \frac{2}{AC} + \frac{2}{BC} \right) x^3 \quad (2)$$

In the tables I have used the symbol  $x'$  for the quotient  $KABC^2t/V^3$ , because it gives the amount of iodine that would be liberated in  $t$  minutes if the solution retained its original composition throughout the experiment. The amount of iodine actually liberated,  $x$ , is naturally less than  $x'$ , because of the decrease in concentration of the reagents as the reaction proceeds.

In calculating K the values of A, B and C denoting respectively the initial quantities of  $KBrO_3$ , KI and HCl have been expressed in the same units as  $x$  (see p. 683); thus  $A = 6KBrO_3$ ,  $B = 2/3KI$ ,  $C = HCl$ , according to the equation:



For instance in the experiments of Table I,  $A = 123$ ,  $B = 65.78$ ,  $C = 95.15$ .

In each table the constant increases slightly as the reaction proceeds; no importance can be attached to this fact, however, as a change of from 0.05 to 0.1 cc of the hundredth-normal arsenite used in the analysis would account for the increase.

### Effect of Bromide

Judson and Walker<sup>1</sup> have shown that potassium bromide, which is one of the products of the reaction between bromic acid and hydriodic acid, is itself oxidized by bromic acid; this reaction, however, takes place much more slowly than the oxidation of potassium iodide even when equivalent quantities are employed, and in the experiments of Tables I to IV the concentration of the bromide never reached 3 percent of that of the iodide. A few experiments in which small quantities of potassium bromide were added to the reacting mixture gave results identical with those in which no such addition had been made, so that it was not necessary to make any correction for the presence of this product of the reaction.

In this connection a number of experiments were undertaken to see whether the two reactions, *viz.*, the oxidation of potassium iodide and that of potassium bromide by bromic acid, take place independently in the solution. In Tables V and VII potassium bromide alone was present; in those of VI and VIII both bromide and iodide, the latter, however, in comparatively small quantity, as under like conditions the iodide is oxidized 58 times as rapidly as the bromide.

In the fourth column of Tables VI and VIII are entered the sums of the values of  $x'$  from Tables I and V, and IV and VII respectively; that is to say, the combined amounts of iodine which would have been liberated in solutions containing the bromide and iodide separately; in each case these sums are greater than the amount of iodine set free in the mixture, as given in column four of Tables VI and VII.

TABLE V  
KBrO<sub>3</sub>, 20.5; KBr, 2000; HCl, 95.15

$t$	$x$	$x'$
20	0.61	0.62
30	0.94	0.95
45	1.42	1.44
60	1.85	1.89
90	2.75	2.86

<sup>1</sup> Jour. Chem. Soc., 73, 411 (1898).

TABLE VI

KI, 20.5; KBr, 2000; I, 98.67; HCl, 95.15

<i>t</i>	<i>x</i>	<i>x'</i> (mixture)	<i>x'</i> (Sum I and V)
20	1.28	1.31	1.52
30	1.87	1.93	2.39
45	2.75	2.87	3.67
60	3.40	3.58	4.84
90	5.31	5.80	7.82

[Note: As the concentrations of the reagents have the same effect on the rate of oxidation of bromide<sup>1</sup> as on that of iodide, the values of *x'* in Tables V and VII were calculated from equation (2).

In calculating *x'* (mixture) for Tables VI and VIII the concentration of the bromide has been regarded as constant, and *x'* has been computed by means of a modified form of equation (2), viz.:

$$x' = x + (1/2A + 1/C)x^2 + (x - y)^2/2B \quad (2 \text{ bis})$$

where *y* is the value of *x* in Table V, and *x - y* is substituted for *x* in the term  $x^2/2B$ , *y* being regarded as the iodine liberated (in experiments VI) by the bromine set free by the action of bromate on bromide, and *x - y* that liberated by direct action of bromate on iodide.]

TABLE VII

KBrO<sub>3</sub>, 20.5; KBr, 2000; HCl, 190.3

<i>t</i>	<i>x</i>	<i>x'</i>
20	2.40	2.46
30	3.76	3.91
45	5.39	5.70
60	7.00	7.50
90	9.71	10.71

<sup>1</sup> Judson and Walker: loc. cit.

TABLE VIII

KBrO <sub>3</sub> , 20.5; KBr, 2000; KI, 98.67; HCl, 190.3			
<i>t</i>	<i>x</i>	<i>x'</i> (mixture)	<i>x'</i> (Sum IV and VII)
20	4.75	5.01	6.20
30	7.35	7.98	9.82
45	10.60	12.02	14.57
60	13.40	15.73	19.10
90	18.58	23.43	28.72

The difference between "*x'* mixture" and "*x'* sum" in Tables VI and VIII was found to be due to the presence of the large quantities of potassium salts, which, as the readings of Tables IX and X show, retard the oxidation of potassium iodide.

The solutions used in the experiments of these two Tables (IX and X) are the same as those of Tables I and IV, with the addition of enough potassium chloride to make the concentration of the potassium ion the same as in the experiments of Tables V and VII. As is shown in the last columns of Tables IX and X, the iodine liberated in solutions containing both iodide and bromide is the sum of that liberated in solutions containing iodide alone, *plus* the iodine equivalent of the bromide liberated in the absence of iodide. Thus, the two reactions—oxidation of iodide by bromic acid, and oxidation of bromide by bromic acid—proceed independently in the same solution.

TABLE IX

KBrO <sub>3</sub> , 20.5; KCl, 2000; KI, 98.67; HCl 95.15				
<i>t</i>	<i>x</i>	<i>x'</i>	<i>x'</i> (Sum V and IX)	<i>x'</i> mixture (VI)
20	0.67	0.68	1.30	1.31
30	1.01	1.03	1.97	1.93
45	1.49	1.54	2.96	2.87
60	1.85	1.93	3.78	3.58
90	2.91	3.10	5.85	5.80



TABLE X

KBrO <sub>3</sub> , 20.5; KCl, 2000; KI, 98.67; HCl, 190.3				
<i>t</i>	<i>x</i>	<i>x'</i>	<i>x'</i> (Sum VII and X)	<i>x'</i> from VIII
20	2.65	2.76	5.22	5.01
30	4.00	4.28	8.19	7.98
45	5.85	6.48	12.18	12.02
60	7.39	8.31	15.81	15.73
90	10.79	13.06	23.77	23.43

This simple relation makes it very easy to allow for the effect of the bromide which is formed from the bromate by the action of hydriodic acid. Judson and Walker have shown that the form of the equation for the rate of oxidation of bromide by bromate is the same as that of my equation 1; and the value of its constant calculated from the experiments of Table V, corrected for the high concentration of the potassium ion, and expressed in my units, is  $2.2 \times 10^{-13}$ .

The bromine formed by the oxidation of the bromide would, of course, react instantaneously with the potassium iodide, and liberate an equivalent amount of iodine, so that the total amount of iodine liberated in the time *t* is governed by the following differential equation, in which *D* represents the number of equivalents of bromide initially present.

$$\frac{dx}{dt} = (A-x)(C-x) \left[ 100 \times 10^{-13}(B-x) + 2.2 \times 10^{-13}(D+x) \right] V^{-3}. \quad (3)$$

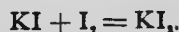
In all the experiments of this paper, except those in which potassium bromide was added at the beginning, *D* = 0, and the last term of equation (3) may be neglected.

#### Effect of Iodine

The only other product of the reaction which might influence the rate is iodine. In order to study its effect I undertook the experiments of Table XI in which iodine was dissolved in the stock solution of potassium iodide and its amount determined by titration.

The first column of the table gives the amount of free iodine initially present in the reacting mixture expressed in

cubic centimeters of 0.010017 normal arsenite; the second, under "KI Corr.," the potassium iodide initially present, which was calculated by subtracting one-half the number in the first column from 98.67 (which was the amount of potassium iodide in the solution before addition of iodine), according to the equation:



Under  $x$  is entered the amount of iodine liberated during the time  $t$  (minutes), obtained by subtracting the initial iodine from the "titration." Under " $x$  calc." is given the amount of iodine that would be liberated in the same time in solutions which contained throughout the experiment the amount of bromate and acid entered at the head of the table, and the amount of potassium iodide entered in the second column under "KI corr.," but no "initial iodine."

It will be noted that the difference between " $x$ " and " $x$  calc." entered in the last column of Table XI, although small, are all positive, and increase with increase in the amount of iodine present. This is in accord with the results of Mr. Dushman's measurements on the rate of oxidation of potassium iodide by iodic acid in the presence of free iodine, and points to the oxidation of triiodion by bromic acid.

The correction for this subsidiary reaction is so small, however, that the relations between concentrations and rate given by equation 2 should hold whether free iodine be present or not, and the equation should be able to account for the whole progress of the reaction between bromic and hydriodic acids from its commencement to its end. This conclusion is borne out by the experiments recorded in Table XLI of the Appendix, for which I am indebted to Mr. F. C. Bowman, where the value of  $K$  remains constant within 1 or 2 percent while 95 percent of the bromate is reduced.

#### Temperature Coefficient

To find the temperature coefficient, I made a series of measurements at 30°, 25° and 0° C.

TABLE XI

KBrO <sub>3</sub> , 20.5;		KI, 98.67;		HCl, 190		
Initial I	KI corr.	<i>t</i>	Titration	<i>x</i>	<i>x</i> calc.	Diff.
0	98.67	60	9.60	9.60	9.52	0.08
0	98.67	90	13.40	13.40	13.31	0.09
0	98.67	120	16.75	16.75	16.66	0.09
7.73	94.80	60	{ 17.07 17.06	9.33	9.15	0.18
7.73	94.80	90	{ 20.68 20.75	12.98	12.80	0.18
7.73	94.80	120	{ 23.88 23.90	16.16	15.99	0.17
11.75	92.80	60	{ 20.75 20.78	9.01	8.94	0.07
11.75	92.80	90	{ 24.70 24.58	12.89	12.56	0.33
11.75	92.80	120	{ 27.78 27.78	16.03	15.75	0.28
16.78	90.28	60	{ 25.77 —	8.99	8.74	0.24
16.78	90.28	90	{ 29.59 —	12.81	12.32	0.49
16.78	90.28	120	{ 32.43 32.50	15.70	15.38	0.32
20.92	88.21	60	{ 29.80 29.82	8.93	8.60	0.33
20.92	88.21	90	{ 33.51 33.46	12.56	12.07	0.49
20.92	88.21	120	{ 36.60 36.42	15.59	15.16	0.43
40.54	78.40	60	{ 48.26 —	7.72	7.60	0.12
40.54	78.40	90	{ 51.46 51.43	10.91	10.74	0.17
40.54	78.40	120	{ 54.70 54.58	14.10	13.51	0.59
52.40	72.47	60	60.05	7.65	7.13	0.52
52.40	72.47	90	{ 63.09 62.94	10.62	10.02	0.60
52.40	72.47	120	{ 65.98 65.86	13.52	12.66	0.86

TABLE XIII  
 KBrO<sub>3</sub>, 20.5; KI, 98.67; HCl, 190.3

t	At 30°				At 25°					At 0°				
	x	x'	R	K.10 <sup>13</sup>	x	x'	R	K.10 <sup>13</sup>	Coeff.	x	x'	R	K.10 <sup>13</sup>	Coeff.
20	3.46	3.67	183	98	2.58	2.70	135	72	1.84	0.65	0.66	33	17	—
30	5.10	5.57	185	99	3.81	4.07	136	72	1.85	0.88	0.89	30	16	1.84
45	7.50	8.55	190	101	5.65	6.23	138	74	1.89	1.30	1.33	29	16	1.87
60	9.60	11.39	189	100	7.29	8.28	138	74	1.87	1.75	1.80	30	16	1.85
90	13.40	17.23	191	102	10.37	12.48	139	74	1.89	2.58	2.70	30	16	1.85
120	16.75	23.45	195	104	13.13	16.75	139	74	1.97	3.38	3.58	30	16	1.87

The average value of the "temperature coefficient" of the rate, or the factor by which the rate is multiplied for a rise of 10° in the temperature, may be found by taking the cube root of the ratio between the rates at 30° and 0° C.; it is 1.85. The coefficients determined from the measurements at 30° and 25° C. (which are entered in the table "at 25°") are practically the same, or if anything, a little higher, see Table XIII.

#### Appendix

Magnanini's experiments, carried out in 1890,<sup>1</sup> some of those of Ostwald's<sup>2</sup> and the experiments of Noyes<sup>3</sup> are here recalculated.

At the head of each table I have given the initial composition of the reacting mixture, the numbers divided by 100,000 denoting gram-formula weights of the reagent initially present, the volume being 10 cc in all of Magnanini's and Ostwald's measurements, while in Noyes' the numbers recorded are for a volume of 1 litre. In all these experiments the temperature was 25° C. Mr. F. C. Bownian's experiments were carried out in this laboratory at 0° C., and the numbers recorded from his experiments are for a volume of 1 litre.

<sup>1</sup> Gazz. chim. Ital., 20, 377 (1890).

<sup>2</sup> Zeit. phys. Chem., 2, 27 (1888).

<sup>3</sup> Ibid., 18, 118 (1890).

In the first column of the tables (under *t*) is entered the duration of the experiments in minutes; in the second, the amount of iodine liberated *x* (in cubic centimeters of *n*/100 thiosulphate); where Magnanini gave the result of duplicate experiments, I have taken the average. In the third and last column I have entered the value of the constant *K* of the equation:

$$\frac{1}{V} \cdot \frac{dx}{dt} = K(A-x)(B-x)(C-x)^2V^{-1}$$

where *A*, *B* and *C* are taken from the heads of the table, and *V* is the volume in litres, *e. g.*, for Table XV, *A* = 11.11, *B* = 7.41, *C* = 24.07, *V* = 0.01. See page 685.

In computing the values of *K*, I made use of "The Method of Areas," described by Mr. R. E. De Lury.<sup>1</sup>

In order to facilitate comparison of the values of *K* so obtained, I have brought them together in the last table. The constants bracketed have been calculated from the experimental data by making use of the temperature coefficient 1.85 obtained from Table XIII. In the experiments where excess of hydrochloric or nitric acid was used, Magnanini's values agree with my own for the same temperature; replacing these monobasic acids by sulphuric acid, takes about 33 percent of *K*, corresponding to a difference of 12 percent in the dissociation, which is a fair agreement with the results of measurements of the electrical conductivity. In the experiments in which the concentration of the hydrion was large, the constants are uniform, here however their concentration is small, the constant shows a falling off. This is in line with the results of Mr. W. C. Bray's experiments on the oxidation of hydrogen iodide by chloric acid.<sup>2</sup>

The values of the constants derived from Ostwald's measurements are somewhat smaller than those from the corresponding measurements of Magnanini. Addition of chloric acid and of hydrobromic acid increases the constant

<sup>1</sup> Jour. Phys. Chem., 10, 425 1906.

<sup>2</sup> Ibid., 7, 92 (1903).

Coef.  
—  
1.84  
1.87  
1.85  
1.85  
1.87

very slightly, due no doubt to the oxidation of the bromion or to the reduction of the chlorate.

Noyes and Scott worked with the potassium salts of bromic acid and hydriodic acid in presence of a constant amount of hydrochloric acid; their constant agrees very closely with my own.

*Magnanini's Measurements*

TABLE XIV  
HBrO<sub>3</sub>, 1.85; HI, 11.11

<i>t</i>	<i>x</i>	$K \times 10^{13}$
5	0.82	142
12	1.44	119
13	1.46	116
21	1.84	100
25	2.05	99
41	2.72	93
52	2.96	91
84	3.69	88
91	3.80	89
175	4.82	86

TABLE XV  
HBrO<sub>3</sub>, 1.85; HI, 11.11; HCl, 11.11

<i>t</i>	<i>x</i>	$K \times 10^{13}$
2	0.82	99
3	1.05	87
9	2.35	84
15	3.27	85
17	3.38	81
28	4.38	84
31	4.50	83
35	4.68	84
40	5.10	86

TABLE XVI  
HBrO<sub>3</sub>, 1.85; HI, 11.11; HCl, 22.22

<i>t</i>	<i>x</i>	$K \times 10^{13}$
2	1.43	85
6	2.98	83
12	4.19	80
17	4.93	80
18	5.06	80
20	5.28	81

TABLE XVII  
HBrO<sub>3</sub>, 1.85; HI, 11.11; HCl, 33.33

<i>t</i>	<i>x</i>	$K \times 10^{13}$
2	2.03	83
4	3.17	82
6	3.93	81
8	4.52	81
10	4.90	80
11	5.08	79

TABLE XVIII  
HBrO<sub>3</sub>, 1.85; HI, 11.11; HCl, 44.44

<i>t</i>	<i>x</i>	$K \times 10^{13}$
2	2.55	68
4	3.94	70
6	4.72	70
7	5.15	72
8	5.33	72

TABLE XIX  
HBrO<sub>3</sub>, 1.85; HI, 11.11; HNO<sub>3</sub>, 22.22

<i>t</i>	<i>x</i>	$K \times 10^{13}$
2	1.37	82
6	2.88	78
12	4.19	77
17	4.84	77
19	5.14	78

TABLE XX  
HBrO<sub>3</sub>, 1.85; HI, 11.11; HNO<sub>3</sub>, 33.33

<i>t</i>	<i>x</i>	K × 10 <sup>13</sup>
2	2.03	77
4	3.06	73
6	3.83	72
8	4.41	72
10	4.89	72
11	5.03	72

TABLE XXI  
HBrO<sub>3</sub>, 1.85; HI, 11.11; HNO<sub>3</sub>, 44.44

<i>t</i>	<i>x</i>	K × 10 <sup>13</sup>
2	2.57	68
4	3.80	67
6	4.60	66
8	5.19	67

TABLE XXII  
HBrO<sub>3</sub>, 1.85; HI, 11.11; H<sub>2</sub>SO<sub>4</sub>, 5.55

<i>t</i>	<i>x</i>	K × 10 <sup>13</sup>
2	0.68	81
9	2.10	71
17	3.07	69
31	4.20	69
46	4.81	67
51	4.94	66
56	5.27	68

TABLE XXIII  
HBrO<sub>3</sub>, 1.85; HI, 11.11; H<sub>2</sub>SO<sub>4</sub>, 11.11

<i>t</i>	<i>x</i>	K × 10 <sup>13</sup>
2	1.04	57
9	2.99	53
20	4.51	52
25	4.87	52
28	5.11	52
31	5.26	52

TABLE XXIV  
HBrO<sub>3</sub>, 1.85; HI, 11.11; HCl, 22.22

<i>t</i>	<i>x</i>	K × 10 <sup>13</sup>
2	1.83	43
9	4.32	39
12	4.95	39
13	5.09	39
17	5.55	38

TABLE XXV  
HBrO<sub>3</sub>, 5.55; HI, 11.11

<i>t</i>	<i>x</i>	K × 10 <sup>13</sup>
2	1.23	106
6	2.55	96
9	3.25	95
12	3.78	94
15	4.23	93
21	4.88	93
23	5.02	95
24	5.02	91
27	5.34	92

TABLE XXVI  
HBrO<sub>3</sub>, 9.26; HI, 11.11

<i>t</i>	<i>x</i>	$K \times 10^{13}$
2	2.30	91
4	3.56	90
6	4.36	89
8	4.94	88
10	5.43	89

TABLE XXVII  
HBrO<sub>3</sub>, 1.85; KBrO<sub>3</sub>, 3.70; HI, 11.11

<i>t</i>	<i>x</i>	$K \times 10^{13}$
2	0.83	116
6	1.85	107
9	2.46	107
12	2.75	99
17	3.41	99
20	3.60	96
28	4.25	96
41	4.86	95
46	5.15	96

TABLE XXVIII  
HBrO<sub>3</sub>, 1.85; KBrO<sub>3</sub>, 9.25; HI, 11.11

<i>t</i>	<i>x</i>	$K \times 10^{13}$
2	1.38	104
6	2.68	88
9	3.36	88
12	3.87	87
18	4.65	87
22	4.97	87
25	5.16	86

*Ostwald's Measurements*

TABLE XXIX  
HBrO<sub>3</sub>, 1.856; HI, 11.11

<i>t</i>	<i>x</i>	$K \times 10^{13}$
1	0.22	—
21	1.89	93
41	2.81	92
81	3.93	94
146	4.83	94
201	5.37	96
301	5.89	96
431	6.36	98

TABLE XXX  
HBrO<sub>3</sub>, 1.856; HI, 11.11; H<sub>2</sub>SO<sub>4</sub>, 5.55

<i>t</i>	<i>x</i>	$K \times 10^{13}$
9	2.04	59
17	3.07	61
31	4.17	63
56	5.27	64
71	5.67	64
97	6.14	65
115	6.39	65



TABLE XXXI

HBrO<sub>3</sub>, 1.85; HI, 11.11; HCl, 11.11

<i>t</i>	<i>x</i>	K × 10 <sup>13</sup>
9	2.46	85
17	3.54	84
31	4.63	84
41	5.20	85
51	5.60	86
61	5.90	87
71	6.20	85

TABLE XXXII

HBrO<sub>3</sub>, 1.85; HI, 11.11; HNO<sub>3</sub>, 11.11

<i>t</i>	<i>x</i>	K × 10 <sup>13</sup>
9	2.44	84
17	3.51	82
31	4.63	82
41	5.18	84
51	5.55	81
61	5.86	80
71	6.09	80

TABLE XXXIII

HBrO<sub>3</sub>, 1.85; HI, 11.11; HClO<sub>3</sub>, 11.11

<i>t</i>	<i>x</i>	K × 10 <sup>13</sup>
9	2.54	90
17	3.54	88
25	4.35	89
33	4.77	88
41	5.18	88
51	5.56	88
61	5.85	89

TABLE XXXIV

HBrO<sub>3</sub>, 1.85; HI, 11.11; HClO<sub>4</sub>, 11.11

<i>t</i>	<i>x</i>	K × 10 <sup>13</sup>
9	2.43	85
17	3.52	82
25	4.25	84
33	4.71	83
41	5.15	84
51	5.56	85
61	5.78	85

TABLE XXXV

HBrO<sub>3</sub>, 1.85; HI, 11.11; H<sub>2</sub>SO<sub>3</sub>, 5.55

<i>t</i>	<i>x</i>	K × 10 <sup>13</sup>
9	2.40	81
17	3.41	80
25	4.16	81
33	4.65	81
41	5.05	81
51	5.40	81
61	5.76	81

TABLE XXXVI

HBrO<sub>3</sub>, 1.85; HI, 11.11; HBr, 11.11

<i>t</i>	<i>x</i>	K × 10 <sup>13</sup>
9	2.59	89
17	3.68	90
25	4.43	92
33	4.94	93
41	5.34	94
51	5.72	95
61	6.04	96

## Noyes' Measurements

TABLE XXXVII TABLE XXXVIII  
 KBrO<sub>3</sub>, 166; KI, 1000; HCl, 4000 KBrO<sub>3</sub>, 83; KI, 500; HCl, 4000

<i>t</i>	<i>x</i>	K × 10 <sup>13</sup>	<i>t</i>	<i>x</i>	K × 10 <sup>13</sup>
2	112	63	1.5	46	65
4	192	62	3	88	68
7	279	62	5	125	66
11	358	62	8	180	70
16	423	62	12	233	70
22	479	62	17	261	72
30	526	62	23	294	73
40	562	62			

TABLE XXXIX TABLE XL  
 KBrO<sub>3</sub>, 83; KI, 1000; HCl, 4000 KBrO<sub>3</sub>, 83; KI, 500; HCl, 4000

<i>t</i>	<i>x</i>	K × 10 <sup>13</sup>	<i>t</i>	<i>x</i>	K × 10 <sup>13</sup>
1.5	48	68	2.5	40	68
3	90	68	5.5	79	68
5	134	68	9	112	72
8	179	65	15	155	71
12	223	63	23	194	72
17	258	60	36	235	74
23	290	60	58	275	71

## F. C. Bowman's Measurements

TABLE XLI  
 KBrO<sub>3</sub>, 55.26; KI, 4960; H<sub>2</sub>SO<sub>4</sub>, 1666.6

<i>t</i>	<i>x</i>	Percent bromate decomposed	K · 10 <sup>11</sup>
6	62.4	18.8	98
19	155.8	46.8	98
30	206.6	62.3	99
40	238.8	72.1	99
50	261	78.7	98
60	276.4	83.3	97
70	290.2	87.6	97
80	299.6	90.2	97
100	315.6	95.1	98

TABLE XLIII  
SUMMARY OF TABLES

Experimenter	Table	Initial Composition (Vol. = one litre)	K × 10 <sup>13</sup> for 30° C	K × 10 <sup>13</sup> 25° C	K × 10 <sup>13</sup> 0° C
Clark:	XIII	KBrO <sub>3</sub> , 82; KI, 394.7; HCl, 760	100	73	16
Magnanini:	XIV	HBrO <sub>3</sub> , 185; HI, 1111	(139)	102	(22)
	XV	" " " "	(117)	86	(19)
	XVI	" " " "	(112)	82	(18)
	XVII	" " " "	(111)	81	(18)
	XVIII	" " " "	(96)	70	(15)
	XIX	" " " "	(107)	78	(17)
	XX	" " " "	(100)	73	(16)
	XXI	" " " "	(92)	67	(15)
	XXII	" " " "	(96)	70	(15)
	XXIII	" " " "	(73)	53	(12)
	XXIV	" " " "	(55)	40	(9)
	XXV	" " " "	(130)	95	(21)
	XXVI	HBrO <sub>3</sub> , 555; " "	(122)	84	(19)
	XXVII	HBrO <sub>3</sub> , 1111; " "	(137)	100	(22)
	XXVIII	HBrO <sub>3</sub> , 185; HI, 1111	(123)	90	(20)
Ostwald:	XXIX	HBrO <sub>3</sub> , 185; HI, 1111	(130)	95	(21)
	XXX	" " " "	(87)	63	(14)
	XXXI	" " " "	(116)	85	(19)
	XXXII	" " " "	(112)	82	(18)
	XXXIII	" " " "	(120)	88	(19)
	XXXIV	" " " "	(115)	84	(18)
	XXXV	" " " "	(111)	81	(18)
	XXXVI	" " " "	(127)	93	(20)
Noyes and Scott:	XXXVII	KBrO <sub>3</sub> , 166; KI, 1000; HCl, 4000	(85)	62	(14)
	XXXVIII	" " KI, 500; HCl, 4000	(94)	69	(15)
	XXXIX	KBrO <sub>3</sub> , 83; KI, 1000; HCl, 4000	(89)	65	(15)
	XL	" " KI, 500; HCl, 4000	(97)	71	(16)
Bowman:	XLI	KBrO <sub>3</sub> , 55.26; KI, 4950; H <sub>2</sub> SO <sub>4</sub> , 1676	(71)	(45)	10

**Summary**

(1) The rate at which iodine is liberated in solutions containing potassium bromate, potassium iodide and hydrochloric acid is proportional to the concentration of the bromate, the concentration of the iodide, and the square of the concentration of the acid.

(2) In solutions containing potassium bromate, iodide, bromide and hydrochloric acid the two haloid salts are oxidized independently.

(3) The potassium triiodide formed by the oxidation of iodide adds very slightly to the rate of reduction of bromate; so that, in first approximation, the effect on the rate produced by the iodine liberated during the reaction may be neglected.

(4) Thus the progress of the reaction may be expressed by a simple differential equation (see equation 1, p. 685), which is shown to be in accordance with the experiments. A term to represent the effect due to the bromide formed during the reaction may be introduced into the equation (see equation 3).

(5) Raising the temperature  $10^{\circ}$  multiplies the rate by 1.85.

(6) The equations developed in this paper have been used to recalculate Magnanini's, Ostwald's and Noyes' measurements. (See Appendix.)

These measurements were carried out in the chemical laboratory of the University of Toronto during the winter of 1904-5; and in conclusion, I wish to express my sincerest thanks to Prof. W. Lash Miller for suggesting this research and for his supervision throughout the work.

*The University of Toronto,*

*June, 1906*

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