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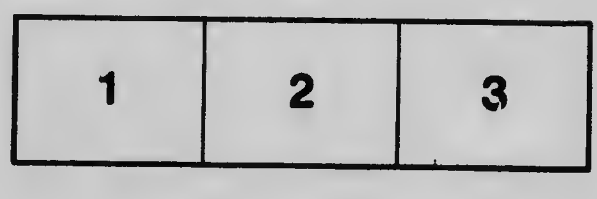

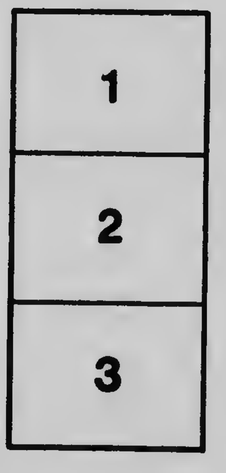

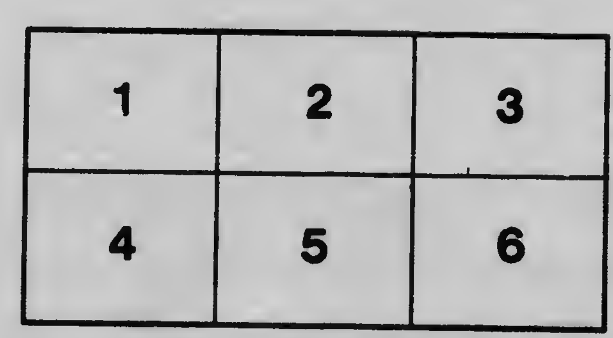

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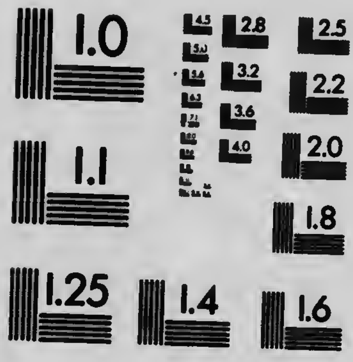
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PAPERS FROM THE CHEMICAL LABORATORIES

No. 65: THE REACTION BETWEEN BROMIC, HYDRIODIC AND ARSENIOUS ACIDS, BY FRED. C. BOWMAN

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THE REACTION BETWEEN BROMIC, HYDRIODIC AND ARSENIOUS ACIDS, AND THE "INDUCTION" BY HYDROGEN BROMIDE OF THE REACTION BETWEEN BROMIC AND ARSENIOUS ACIDS

BY FRED C. BOWMAN

The reduction of bromates by bromides or iodides in acid solution has been studied by Ostwald,[1] Burchard,[2] Meyerhoffer,[3] Scott and Noyes,[4] Magnanini,[5] Judson and Walker,[6] Schilow,[7] and lastly by Mr. R. H. Clark.[8] The net result of these researches is that the rate is proportional to the first power of the concentration of the bromate, the first power of that of the bromide or iodide, and the second power of that of the acid.

The ordinary chemical equations for the reactions of the bromate with the bromide and iodide are:

$$\begin{aligned} KBrO_3 + 5KBr + 3H_2SO_4 &= 3K_2SO_4 + 3Br_2 + 3H_2O \\ KBrO_3 + 6KI + 3H_2SO_4 &= 3K_2SO_4 + 3I_2 + 3H_2O + KBr \end{aligned} \qquad (1)$$

or in the ionic notation:

$$\begin{aligned} BrO'_3 + 9Br' + 6H^{\bullet} &= Br' + 3Br'_3 + 3H_2O \\ BrO'_3 + 9I' + 6H^{\bullet} &= Br' + 3I'_3 + 3H_2O \end{aligned} \qquad (2)$$

Since these do not square with the kinetic hypothesis, which demands equations of the form

$$BrO'_3 + Br' + 2H^{\bullet} = \text{(products of the reaction)} \qquad (3)$$

resort has been had to the usual method of "explaining" discrepancies between theory and practice in kinetic measurements, by assuming the temporary existence of hypothetical intermediate compounds, such as the HBrO and $HBrO_2$ of the following equation.

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[1] Zeit. phys. Chem., **2**, 127 (1888).

[2] Ibid., **2**, 796 (1888).

[3] Ibid., **2**, 585 (1888).

[4] Ibid., **18**, 128 (1895).

[5] Gazz. chim. Ital., **20**, 390 (1890).

[6] Jour. Chem. Soc., **73**, 410 (1898).

[7] Zeit. phys. Chem., **27**, 512 (1898); **42**, 641 (1903).

[8] Jour. Phys. Chem., **10**, 679 (1906).

$$BrO'_3 + Br' + 2H^{\cdot} = HBrO_2 + HBrO \qquad (4)$$
$$BrO'_3 + I + 2H = HBrO_2 + HIO$$

Independent evidence of the formation of these intermediate acids would, of course, be very welcome;[1] and even the confirmation by experiment of conclusions based on the assumption that they exist would be of value.

One such conclusion has been drawn by Luther,[2] who points out that compounds which *ex hypothesi* react quickly with certain reducing agents, may naturally be expected to [illegible] quickly with others; and suggests that new cases of chemical induction are apt to be found by a study of the reactions whose kinetic equations lead to the assumption of such hypothetical "primary" products.

The only induced reaction in which bromic and hydrobromic acids are known to take part, is that in which arsenious acid acts as acceptor; and, in accordance with the view just set forth, the induction is ascribed—both by Luther and by Schilow who discovered the reaction—to the oxidation of the arsenious acid by the hypothetical primary products of Equation 4.

It is not necessary, however, to have recourse to these hypothetical acids in order to account for the results of Schilow's measurements. The bromine liberated by the oxidation of the hydrogen bromide (Equation 1) acts instantaneously on arsenious acid, and all the experimental data are in full accord with the assumption that the "induced" oxidation of arsenious acid is due to this action alone.[3] There are thus two explanations of Schilow's measurements available. The first of them is in accordance with the explanation offered for the kinetics of the reaction between bromic and hydrobromic acids, and at first sight seems to afford it independent support; but the second accounts for all that is known of the induction without the assumption of any hypothetical mechanism whatever.

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[1] Ostwald: Lehrbuch II, (2) 243 (1902).

[2] Zeit. phys. Chem., 46, 817 (1903).

[3] Ibid., 42, 670 (1903).

In order to throw more light on the matter, I have studied the oxidation of arsenious acid in solutions containing bromic and hydriodic acids. In this case, the final product—iodine—does not react instantaneously with the arsenious acid, but slowly, according to known laws; so that if any arsenious acid were oxidized by the hypothetical intermediate acids, or in any other way than by the iodine formed in the reaction, the fact could be established, and the amount ascertained. My work has been much facilitated by the circumstance that the reaction between bromic and hydriodic acid and that between arsenious acid and iodine have already been studied in this laboratory by Mr. Clark[1] and Mr. Roebuck[2] respectively. This has enabled me to plan my experiments so that very little arsenious acid was oxidized by the iodine; any action of the hypothetical oxyacids would therefore readily be detected.

The reaction was carried out in a thermostat at 0° to 0.2°; the burettes and pipettes were calibrated by myself, and the solutions of arsenious acid, potassium iodide, potassium bromate, iodine and sodium thiosulphate were made from pure chemicals and standardized in the usual way. The iodide in the iodine solution was allowed for in calculating the concentration of the iodion.

In the tables and in the calculations, the amount of each reagent is expressed in cubic centimeters of hundredth-normal solution. Thus the number after $KBrO_3$ multiplied by $^1/_6 \times 167.1 \times 10^{-5}$ gives the number of grams of potassium bromate; the number after KI multiplied by $^3/_2 \times 166 \times 10^{-5}$ gives the number of grams of potassium iodide; the number after KBr multiplied by $^3/_2 \times 119.1 \times 10^{-5}$ gives the number of grams of potassium bromide; the number after H_2SO multiplied by $^1/_2 \times 98.08 \times 10^{-5}$ gives the number of grams of sulphuric acid; the number after I multi-

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ur. Phys. Chem., 10, 679 (1906).

bid., 6, 365 (1902); 9, 727 (1905).

plied by 126.85×10^{-5} gives the number of grams of free iodine, and that after As_2O_3 multiplied by $^1/_4 \times 198 \times 10^{-5}$ the number of grams of arsenious acid. After *Vol.* is given the volume in liters in which these amounts of the reagents were dissolved.

The duration of the reaction, in minutes, is stated under t; the number of grams of bromate reduced may be found by multiplying the number under x by $^1/_6 \times 167.1 \times 10^{-5}$; and the number of grams of arsenious acid oxidized to arsenic acid, by multiplying the number under y by $^1/_4 \times 198 \times 10^{-5}$. In solutions containing both bromate and arsenious acid, therefore, the quantity of free iodine in the solution is represented by $x - y$.

The measurements fall naturally into three series.

Series I. The Effect of Arsenious Acid on the Reaction between Bromic and Hydriodic Acids

First of all it was necessary to know whether addition of arsenious acid affects the rate at which bromic acid is reduced by hydrogen iodide. For this purpose parallel sets of measurements were made, one in the presence of arsenious acid and one in its absence, all the other reagents being of the same concentrations in both.

The solutions of potassium bromate, potassium iodide and sulphuric acid were mixed in a large stoppered bottle, and at intervals samples were pipetted out, rendered alkaline with ammonium bicarbonate, and titrated with centinormal arsenious acid. The measurements are recorded in Tables I, II and III.

From each pair of numbers (x, t) so obtained, the value of the constant K_1 of the equation[1]

$$dx/dt = K_1(KBrO_3 - x)(KI - x)(H_2SO_4 - x)^2(Vol)^{-3} \qquad (5)$$

was calculated as follows. A curve was plotted on section paper with x and the right hand member of Equation 5 as coördinates, and the areas under the curve were measured. For each value of x the corresponding value of

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[1] Clark: loc. cit.

$$K_1(\mathrm{Vol})^{-3}\int dt/dx.dx = K_1t(\mathrm{Vol})^{-3} \tag{6}$$

was thus obtained; and from this the value of K_1 itself, by division by $(Vol)^{-3}\ t$. This method, which was suggested by Prof. Lash Miller, is perhaps the easiest way to determine K from a series of values of x and t, when the form of the differential equation is known.

TABLE I

$KBrO_3$, 199; KI, 1984; H_2SO_4, 2000; Vol., 0.600
(75 cc titrated)

t	x in 75 cc	$K_1 \times 10^{15}$
6	4.68	974
19	11.76	989
30	15.50	997
40	17.92	997
50	19.58	945
60	20.73	969
70	21.77	980
80	22.48	982
90	22.82	930
100	23.68	1041
	Average	980

TABLE II

$KBrO_3$, 199; KI, 1984; H_2SO_4, 4000; Vol., 0.600
(75 cc titrated)

t	x in 75 cc	$K_1 \times 10^{15}$
3	7.40	805
6	12.37	825
9	15.73	807
12	18.18	809
15	19.87	809
18	21.25	823
21	22.15	798
	Average	810

TABLE III

$KBrO_3$, 199; KI, 3968; H_2SO_4, 2000; Vol., 0.600
(75 cc titrated)

t	x in 75 cc	$K_1 \times 10^{15}$
5	6.95	928
10	11.52	905
15	14.84	903
20	17.28	901
25	19.17	909
30	20.42	909
	Average	909

Comparison of Tables I, II and III with Tables VIII, IX and X

t	x		$K_1 \times 10^{13}$	
	I	VIII	I	VIII
6	4.68	4.82	974	—
12	(8.41)	8.34	—	—
18	(11.25)	11.13	—	—
24	(13.62)	13.59	—	—
30	15.50	15.31	997	977
36	(16.98)	16.88	—	—
42	18.28	18.38	—	—
		Average	980	984

t	x		$K_1 \times 10^{13}$	
	II	IX	II	IX
3	7.40	7.45	805	828
6	12.37	12.07	825	797
9	15.73	15.44	807	789
12	18.18	17.99	809	793
15	19.87	19.81	809	796
18	21.25	21.05	823	783
21	22.15	22.63	798	—
		Average	810	798

t	x		$K_1 \times 10^{13}$	
	III	X	III	X
5	6.95	7.08	928	—
10	11.52	11.75	905	935
15	14.84	14.90	903	909
20	17.28	17.43	901	917
25	19.17	19.15	909	901
30	20.42	20.55	909	911
		Average	909	911

When arsenious acid is present (Tables VIII, IX and X) the kinetic equation must be modified somewhat, because of the regeneration of acid and iodide by the action of iodine on arsenious acid:

$$HAsO_3 + I_2 + H_2O = HAsO_4 + 2HI \qquad (7)$$

The amount of iodide present at any moment is thus no longer represented by $KI-x$, as in Equation 5, but by $KI-x-y$, where y is the number of units of arsenious acid oxidized; similarly the acid present at any moment is given by H_2SO_4-x-y. Thus the kinetic equation becomes:

$$dx/dt = K_1(KBrO_3 - x)(KI - x - y)(H_2SO_4 - x - y)^2(Vol)^{-3} \qquad (8)$$

As in my experiments both KI and H_2SO_4 were large in comparison with x and y, the terms $KI-x-y$ and H_2SO_4-

$\overline{x-y}$ were nearly constant, and it was found convenient to replace them by their "effective averages" determined as follows at the suggestion of Mr. R. E. DeLury.[1] A curve was plotted with $x-y$ as ordinates and t as abscissae, using the values found by experiment. The area under this curve between $t = 0$ and $t = t'$, divided by t', is the "effective average" of $x-y$ from the beginning of the experiment to the moment t_1. This function may be written $X-Y$, and is defined by the relation:

$$X-Y = \frac{1}{t'} \int_0^{t'} \overline{x-y}\, dt \tag{9}$$

Introducing these "effective averages" into Equation 8, and integrating:

$$K_1 t' (KI - \overline{X-Y})(H_2SO_4 - \overline{X-Y})^2 \; (Vol)^{-3} = log\ nat\ \frac{KBrO_3}{KBrO_3 - x} \tag{10}$$

The values of K_1 entered in Tables VIII, IX and X were calculated from x and t by means of this equation.

The values of K_1 so obtained from experiments in which arsenious acid was present and from others in which it was not, are collected after Table III; the comparison shows clearly that the rate at which bromic acid is reduced by hydriodic acid is not affected by the presence of arsenious acid, and that the slight apparent acceleration is due to the formation of acid and iodide which accompanied the oxidation of the arsenious acid.

Series II. The Oxidation of Arsenious Acid by Iodine and the Effect of Hydrobromic Acid on the Rate of this Reaction

The rate of the reaction between arsenious acid and iodine has been thoroughly studied by Roebuck; but as my experiments were made with concentrations outside the range of Roebuck's measurements, I thought it better to undertake a new series of my own, rather than rely on an extrapolation from his tables. New measurements were also needed to ascertain what effect, if any, the presence of bromides might exert on the rate.

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[1] See Jour. Phys. Chem., 10, 423 (1906).

The solutions were mixed in a stoppered bottle, and at intervals a sample was pipetted out and analyzed. The method of analysis was that used by Roebuck, *viz.*, rapid titration with centi-normal thiosulphate without dilution or neutralization.

TABLE IV

As_2O_3, 200; KI, 2197; I, 198;
H_2SO_4, 2000; Vol., 0.600
(50 cc titrated)

t	$I - y$ in 50 cc	$K_2 \times 10^{-4}$
2	15.68	169
7	14.88	154
12	14.08	159
17	13.44	155
22	13.03	140
27	12.67	133
32	12.27	130
37	11.56	142
42	11.06	145
52	10.41	143
72	9.27	140

TABLE V

As_2O_3, 200; KI, 2250; I, 247.3;
H_2SO_4, 4002; Vol., 0.600
(50 cc titrated)

t	$I - y$ in 50 cc	$K_2 \times 10^{-4}$
16	18.75	177
30	17.51	166
45	16.65	159
60	15.70	156
75	14.95	156
90	14.25	152
105	13.68	151
120	13.15	150
135	12.64	150
150	12.17	150

TABLE VI

As_2O_3, 200; KI, 3968; I, 197; H_2SO_4, 2000; Vol., 0.600
(75 cc titrated)

t	$I - y$ in 75 cc	$K_2 \times 10^{-4}$
30	22.58	132
60	20.92	135
90	19.34	135
120	18.11	133
150	17.03	133
180	15.96	136
	Average	134

Table IV contains measurements with solutions of approximately the same concentrations as those of Table VIII in which bromic acid was used. Similarly Table V is parallel to Table IX and Table VI to Table X. The experiments of Table VI*A* were undertaken to find whether the decrease in the constant[1] K_2 of the kinetic equation[2]

$$dy/dt = \frac{K_2(I-y)(As_2O_3-y)(Vol)^2}{(KI-y)^2(H_2SO_4-y)} \qquad (11)$$

was due to the fall in the concentration of the iodine or to that of the arsenious acid.

TABLE VI*A*

As_2O_3, 100; I, 197; KI, 1984; H_2SO_4, 4000; Vol., 0.600
(75 cc titrated)

t	I − *y* in 75 cc	$K_2 \times 10^{-4}$
20	23.31	—
40	22.03	—
60	20.92	155
80	20.17	142
100	19.29	145
120	18.61	143
140	18.11	143

TABLE VII

As_2O_3, 200; I, 247.5; KI, 2250; H_2SO_4, 4002; KBr, 200; Vol., 0.600
(50 cc titrated)

t	I − *y* in 50 cc	$K_2 \times 10^{-4}$
45	16.92	139
60	16.08	139
75	15.25	140
90	14.52	141
105	13.92	138
120	13.52	133
135	13.00	135
150	12.52	136

Table VII contains the results of measurements made in solutions containing six times as much bromide as was formed from the bromate in any of my experiments. The rate is noticeably (10-15 percent) less than in the experiments of Table V in which—apart from the bromide—the concentrations were the same; but it is evident that the retardation due to the bromide formed during an experiment may be neglected.

Further measurements of the rate of oxidation of arsenious acid by iodine are furnished by the latter part of Table IX; for although bromic acid was present initially, it was practically all reduced in the first half hour, and from then on the only reaction taking place in the solution was the oxidation of arsenious acid by iodine. The constant K_2 in Table IX was thus determined for the very solution in which the bromic acid had been reduced, $t = 70$ was taken as the initial point.

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[1] K'_2 was computed in the same manner as K'_1 of Tables I and II, by plotting a curve with *y* as abscissae and $K'_2(Vol)^2dt/dy$ as ordinates.

[2] Roebuck: loc. cit.

Series III. The Rate of the Reaction between Bromic, Hydriodic, and Arsenious Acids

For these experiments the reagents were mixed two by two—the arsenious acid and sulphuric acid solutions in one bottle and the potassium bromate and potassium iodide solutions in another. Both were kept in the thermostat, and for each experiment a certain amount of each was pipetted into a small stoppered bottle; the mixture was allowed to react for a measured time, and was then analyzed.

Before determining the iodine and arsenious acid in the product of the reaction, it is, of course, necessary to stop the reaction, or at least to slow it up so much that no appreciable change in the composition of the solution takes place during the progress of the analysis. In the present instance this is a difficult matter. Neutralization of the acid, or dilution of the solution, which stop or retard the liberation of iodine, accelerate its reaction with the arsenious acid; and it was only after many trials and calculations, based on the researches of Roebuck and of Clark, that the following method was perfected.

The mixture to be analyzed (75 cc in volume) was thrown into 450 cc of ice-cold water containing enough thiosulphate to remove all the iodine but one cubic centimeter (centinormal) or less. The remaining iodine was titrated in two minutes with centi-normal thiosulphate and starch by daylight or by the light of an Auer mantle, but not by gaslight. Enough ammonium bicarbonate was added to make the solution alkaline, and finally the arsenious acid was estimated with iodine.

Under these conditions, and when the diluted mixture contains before titration 1 cc $n/100$ iodine, 25 cc $n/100$ arsenious acid, 15 cc $n/1$ sulphuric acid and 4 cc of $F/1$ potassium iodide, a correction of about 0.03 cc $n/100$ must be added to the thiosulphate reading and to the iodine reading in the arsenite determination. This correction must be doubled if only half as much acid be present, and it varies roughly as the square of the excess of iodine not removed by the thiosulphate added to the water of dilution. If by mischance more thiosulphate has been added in dilution than is equivalent to the free iodine, this correction must not be applied.

If much bromic acid remains unreduced, iodine is liberated by it during the first titration. With the above mentioned concentrations of the various reagents, 25 cc *n*/100 bromic acid frees 0.02 cc *n*/100 iodine.

The error of the determinations is greater than the corrections, owing to the difficulty of making sure of the end-point with thiosulphate at such great dilution. This is the weakest point in the method of analysis adopted.

The results of three sets of experiments, with different concentrations of acid and iodide, are given in Tables VIII IX and X.

TABLE VIII

$KBrO_3$, 199; KI, 1984; H_2SO_4, 2000; As_2O_3, 200; Vol., 0.600
(75 cc titrated)

t	$x - y$ in 75 cc	$As_2O_3 - y$ in 75 cc	x	x calc.[1]	y	y calc.[2]	$K_1 \times 10^{15}$
6	4.60	24.78	4.82	4.63	0.22	0.23	1020
12	7.56	24.22	8.34	8.30	0.78	0.79	985
18	9.57	23.44	11.13	11.21	1.56	1.57	972
24	11.24	22.65	13.59	13.52	2.35	2.52	985
30	12.36	22.05	15.31	15.37	2.95	3.37	977
36	12.76	20.88	16.88	16.91	4.12	4.25	968
42	13.05	19.67	18.38	18.31	5.33	5.31	984

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[1] Calculated by use of $K'_1 = 980 \times 10^{-15}$ from Table I.

[2] K'_2 varies with the concentration of the arsenious acid. Hence for the calculation of each number of the column, a value of K'_2 corresponding to the same concentration of arsenious acid was chosen from Table IV, viz: 158 for the first three, 150 for $t = 30$, and 145 for $t = 36$ and $t = 42$.

TABLE IX

KBrO$_3$, 199; KI, 1980; H$_2$SO$_4$, 4000; As$_2$O$_3$, 200; Vol., 0.600
(75 cc titrated)

t	$x-y$ in 75 cc	As$_2$O$_3-y$ in 75 cc	x	x calc.[1]	y	y calc.[2]	K$_1\times10^{15}$	K$_2\times10^{-4}$
3	7.28	24.83	7.45	7.43	0.17	0.10	828	—
6	11.74	24.67	12.07	12.22	0.33	0.32	797	—
9	14.92	24.48	15.44	15.68	0.52	0.68	789	—
12	17.00	24.01	17.99	18.15	0.99	1.06	793	—
15	18.38	23.57	19.81	19.93	1.43	1.50	796	—
18	19.21	23.16	21.05	21.06	1.84	1.98	783	—
21	20.20	22.57	22.63	22.18	2.43	2.45	—	—
24	20.40	22.04	23.36	22.88	2.96	2.95	—	—
70	16.52	16.77	—	—	8.23	—	—	—
80	15.77	15.90	—	—	9.10	—	—	—
90	15.25	15.27	—	—	9.73	—	—	137[3]
100	14.73	14.73	—	—	10.27	—	—	129
110	13.79	14.04	—	—	10.96	—	—	135

TABLE X

KBrO$_3$, 199; KI, 3968; H$_2$SO$_4$, 2000; As$_2$O$_3$, 200; Vol., 0.600
(75 cc titrated)

t	$x-y$ in 75 cc	As$_2$O$_3-y$ in 75 cc	x	x calc.[4]	y	y calc.[5]	K$_1\times10^{15}$
5	7.04	24.96	7.08	6.84	0.04	0.06	—
10	11.58	24.83	11.75	11.52	0.17	0.22	935
15	14.52	24.62	14.90	14.88	0.38	0.43	909
20	5.68	24.25	17.43	17.33	0.75	0.70	917
25	18.13	23.98	19.15	19.24	1.02	0.99	901
30	19.13	23.58	20.55	20.52	1.42	1.31	911
35	19.80	23.28	21.52	21.53	1.72	1.63	906
40	20.09	22.96	22.13	22.30	2.04	2.01	—
						Average	911

The constant K_1, referring to the rate of reduction of the bromic acid (Equation 8), was calculated as described on page 298.

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[1] $K'_1 = 810 \times 10^{-15}$ (Table II).

[2] Values of K'_2 from Table V.

[3] K'_2 calculated from $t = 70$ as initial point; see page 300.

[4] $K_1 = 909 \times 10^{-15}$, for Table III.

[5] $K_2 = 134 \times 10^4$, from Table VI.

The rate of oxidation of the arsenious acid by the iodine liberated during the reaction may be expressed by the equation

$$dy/dt = \frac{K_2(x-y)(As_2O_3-y)(Vol)^2}{(KI-x-y)^2(H_2SO_4-x-y)} \qquad (12)$$

and values of K_2 might be computed by substituting for x and y their "effective averages" and integrating as explained on page 298; the terms involving x and y being almost constant, there is no *petitio principii* in this procedure. It was thought better, however, to calculate y for each measurement of the table, using Equation 12 and the values of K_2 from Tables IV, V and VI. Similarly, the values of "*x calc*" are obtained by the use of K_1 of Tables I, II and III.

The calculated and observed values of x and of y are entered in adjoining columns in Tables VIII to X; the differences are sometimes positive and sometimes negative but in no case exceed the error of analysis; that is, the arsenious acid actually oxidized is just what was acted on by the iodine liberated during the reaction, none has been oxidized by the hypothetical primary products of the reduction of the bromic acid. If these intermediate products had been quantitatively reduced by the arsenious acid (as has been assumed in the case of the analogous reaction with hydrogen bromide) the arsenious acid oxidized would have been from three times to seventy times as much as that actually observed, while the iodine liberated would have fallen to zero.

Conclusions

In solutions containing bromic hydriodic and arsenious acids, no arsenic is oxidized except by the action of the iodine liberated during the reaction; and the rate of reduction of the bromic acid, and the rate of liberation of iodine are unaffected by the presence of arsenious acid, except in so far as the oxidation of the latter by the iodine affects the concentrations of acid and iodide in the solution.

The action of hydrogen iodide on bromic acid, therefore, does not "induce" the oxidation of arsenious acid; and there is no ground for regarding the oxidation of arsenious acid in mixtures of bromic and hydrobromic acids as a case of chemical induction.

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The University of Toronto,
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