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ON THE SPEED OF THE LIBERATION OF IODINE IN MIXED SOLUTIONS OF POTASSIUM CHLORATE, POTASSIUM IODIDE, AND HYDROCHLORIC ACID.

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A systematic study of the conditions of experimentation that determine the progress of a reaction has until of late years received very little attention. During the last two decades, the speed of various reactions as dependent upon modifying influences has been specially investigated, and to-day the subject of chemical dynamics furnishes many interesting problems for investigation. The present work has been undertaken with the view of collecting data for the solving of some of these problems.

Burchard[2] studied the speed of the liberation of iodine in mixtures of hydriodic and iodic acids in very dilute solutions. Similarly he investigated mixtures of hydriodic acid with bromic or chloric acids. Mixtures of the salts of hydriodic and chloric acids with hydrochloric acid, however, have never to my knowledge been investigated in this way. It is the purpose of this paper to study the speed of the liberation of iodine in such mixtures as are influenced: first, by temperature; second, by degree of concentration; third, by the presence of an excess of one or more of the components; and fourth, by the addition of an excess of other acids.

[1] A thesis submitted for the degree of Bachelor of Science in the General Science Course, University of Wisconsin, June, 1894.

[2] Ueber die Oxydation des Jodwasserstoffes durch die Sauerstoffsaüren der Salzbilder, Zeitschr. physik. Chem., 2; p. 796. (1888.)

Preliminary Experiments.— It is well known that when potassium iodide, potassium chlorate, and hydrochloric acid are mixed in solution, iodine is liberated according to this reaction,—

$$K\,Cl\,O_3 + 6\,H\,Cl + 6\,K\,I = 7\,K\,Cl + 3\,H_2\,O + I_6.$$

In order to ascertain the conditions favorable for studying the speed of the liberation of iodine in such mixtures, several preliminary experiments on the effects of temperature and concentration became necessary.

It was found that in mixtures containing equivalents[1] of the salts according to the foregoing reaction as deci-normal solutions at 0° C., iodine is liberated very slowly, a sample of twenty cubic centimeters of the mixture after twenty-four hours requiring only one-tenth cubic centimeter of a deci-normal solution of sodium thiosulphate to destroy the blue color produced by the addition of starch paste.

The same mixture at 100° C. proved well adapted for investigation, as the following table shows:—

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2\,S_2\,O_3$ used in each titration.	Per cent. of Iodine liberated
15	20	1.45	3.6
35	20	3.1	7.8
60	20	4.3	10.8
90	20	6.0	15.0

Preparation of Solutions.—The solutions used were prepared as follows: A normal solution of potassium iodide free from iodate served throughout the investigation. It

[1] Whenever this term is used it is understood to mean equivalents according to the reaction already given.

was prepared by dissolving 165.54 g. of the pulverized salt, dried at 100° C., and making it up to one liter. The normal hydrochloric acid was standardized on calcite. The potassium chlorate was tested for sulphates, nitrates, chlorides, the heavy metals, and the alkaline earths, and found to be pure. The solution of this salt was three times normal and was prepared by taking 61.25 g. of the dry crystallized salt to a liter. A twentieth normal solution of sodium thiosulphate served for titration. It was prepared by dissolving 12.4 g. of the pure crystallized salt per liter of water. The strength of this solution was verified by testing with deci-normal iodine solution. The starch paste used was quite dilute and was prepared by stirring up two to three grams of the fine starch with cold water. Three to four hundred cubic centimeters of boiling hot water were then added and the mixture well stirred. This paste was then filtered, and the filtrate used as indicator. A fresh solution was frequently prepared.

Conduct of Experiments.—The entire series of investigations was conducted at 100° C. The mixtures were prepared by measuring out the desired equivalents of the different components, cooling them to 0° C. in ice water, and then mixing them. Samples of 20 cc. of the mixture were then quickly taken out and put into ordinary six-inch test tubes. The tubes were quickly sealed, but all the time kept as cool as possible. The samples were then plunged into a large kettle of boiling water and kept at this temperature. At definite intervals samples were taken out and plunged into ice water, thus quickly checking the reaction. After one minute the test tubes were broken, washed with cold water, and the iodine determined by means of a twentieth normal solution of sodium thiosulphate.

The test tubes were sealed at about the same distance from the end, thus keeping the pressure nearly constant. Whenever it was found expedient to work with samples of 10 cc., the tubes were used over again. As the test tubes were new, special precautions in cleaning had to be exercised. To remove the alkalies that are given off by new glassware, I followed the advice of Professor Ostwald and steamed the tubes for about five minutes by means of an apparatus figured on p. 295 of his "Hand- und Hilfsbuch zur Ausführung physico-chemischer Messungen."

In mixtures where the components enter in equivalent proportions it was found that the free iodine began to crystallize out when about 40 per cent. had been liberated. To get this iodine into solution a few cubic centimeters of a strong potassium iodide solution were added. But as this excess of potassium iodide might possibly enter into the reaction and so slightly increase the amount of sodium thiosulphate used, the iodine of several samples was shaken out with carbon bisulphide and determined. A comparison of results obtained by these two methods,[1] shows that the addition of a few cubic centimeters of cold potassium iodide during titration has little or no effect on the result.

The equation expressing the reaction shows that for every molecule of potassium iodide present one atom of iodine is liberated. In titrating the iodine with sodium thiosulphate the following reaction takes place,—

$$2\ Na_2\ S_2\ O_3 + I_2 = Na_2\ S_4\ O_6 + 2\ Na\ I.$$

Hence the per cent. of iodine liberated at any time from the given sample, originally containing 20 cc. of potassium iodide in deci-normal solution, is obtained by dividing by forty the number of cubic centimeters of sodium thiosulphate used, the thiosulphate being twentieth-normal.

Presentation of Results.—The results obtained are divided into five sections. Section A includes the results obtained from a mixture containing equivalents of the salts as decinormal solutions. The effect of a definite excess of *one* of the several components upon the speed of the reaction

[1] Sec. B, III, series (1) and (3), and Sec. C, series (4).

is shown in section B. Section C, similar to B, gives the effect upon the speed when definite excesses of *both* potassium iodide and hydrochloric acid are used. Section D gives the results obtained from mixtures containing equivalents of the components in fifth normal and two-fifth normal solutions respectively. The acceleration in the speed by various organic and inorganic acids forms the fifth and last section of the results.

To facilitate comparison, the results obtained in similar series are graphically represented in the same figure. In plotting the curves the axis of abscissas was chosen to denote the time of the reaction, each space representing one hundred minutes, while the percentages of iodine liberated are plotted on the axis of ordinates.

SECTION A.

Series in which equivalents of $K\,Cl\,O_3$, $H\,Cl$, and $K\,I$ enter in deci-normal solutions,[1] *according to the reaction,—*

$$K\,Cl\,O_3 + 6\,H\,Cl + 6\,K\,I = 7\,K\,Cl + 3\,H_2\,O + I_6.$$

A sample of 400 cc. of the mixture was prepared as follows:

Normal Hydrochloric Acid	40.0 cc.
Normal Potassium Iodide	40.0 cc.
Three times normal Potassium Chlorate	13.3 cc.
Water	306.7 cc.
	400.0 cc.

---

[1] Curve A, Figures 1, 2, 3, 5.

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2S_2O_3$ used in each titration.	Per cent. of Iodine liberated.
15	20	1.45	3.6
35	20	3.1	7.8
35	20	3.0	7.5
60	20	4.3	10.8
70	20	4.6	11.5
90	20	6.0	15.0
110	20	6.6	16.5
150	20	7.85	19.6
210	20	9.4	23.5
300	20	12.05	30.1
300	20	12.25	30.6
360	20	13.55	33.9
440	20	14.55	36.4
520	20	15.55	38.9
585	20	16.0	40.0
730	20	17.0	42.5
830	20	18.4	46.0
1250	20	21.3	53.3
1400	20	21.7	54 3
1830	20	23.2	58.0
2000	20	24.1	60.3

SECTION B.

Series in which an excess of one of the three components enters, both of the other components remaining tenth normal.

I. Potassium chlorate in excess. (1) An excess of *one* molecule of $K\,Cl\,O_3$ enters,[1]—

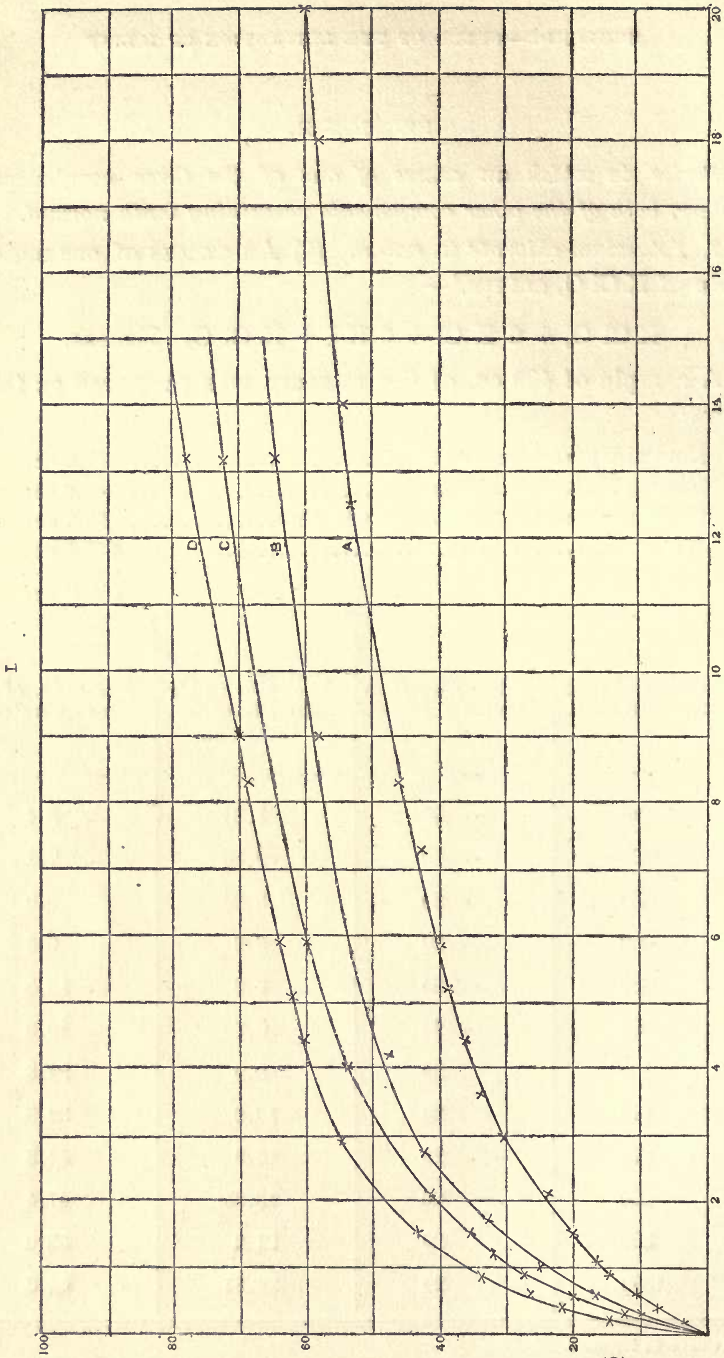
$$K\,Cl\,O_3 + 6\,H\,Cl + 6\,K\,I + K\,Cl\,O_3 \quad \text{Excess.}$$

A sample of 400 cc. of the mixture was prepared as follows:

Normal Hydrochloric Acid	40.0 cc.
Normal Potassium Iodide	40.0 cc.
Three times normal Potassium Chlorate	26.7 cc.
Water	293.3 cc.
	400.0 cc.

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2\,S_2\,O_3$ used in each titration.	Per cent. of Iodine liberated.
10	20	1.35	3.4
20	20	2.85	7.1
30	20	3.95	9.9
30	20	3.9	9.8
60	20	6.6	16.5
60	20	6.7	16.8
100	20	9.9	24.8
170	20	13.0	32.5
270	20	16.9	42.3
420	20	18.95	47.4
590	20	21.2	53.0
1320	20	25.85	64.6

[1] Curve B, Figure 1.


I
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80
100

(2) An excess of *two* molecules of $KClO_3$ enters,[1]—

$$KClO_3 + 6\ HCl + 6\ KI + 2\ KClO_3 \text{ Excess.}$$

A sample of 400 cc. of the mixture was prepared as follows:

Normal Hydrochloric Acid	40 cc.
Normal Potassium Iodide	40 cc.
Three times normal Potassium Chlorate	40 cc.
Water	280 cc.
	400 cc.

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2S_2O_3$ used in each titration.	Per cent. of Iodine liberated.
15	20	2.8	7.0
30	20	5.0	12.5
55	20	8.0	20.0
85	20	10.95	27.4
120	20	12.7	31.8
150	20	14.25	35.6
210	20	16.65	41.6
400	20	21.45	53.6
590	20	23.9	59.8
1320	20	28.95	72.4

After keeping 48 hours at the ordinary temperature of the laboratory 20 cc. of this mixture required 0.4 cc. of twentieth normal sodium thiosulphate solution.

[1] Curve C, Figure 1.

(3) An excess of *three* molecules of $K\,Cl\,O_3$ enters,[1]—

$$K\,Cl\,O_3 + 6\,H\,Cl + 6\,K\,I + 3\,K\,Cl\,O_3 \text{ Excess.}$$

A sample of 400 cc. of the solution was made up as follows:

Normal Hydrochloric Acid	40.0 cc.
Normal Potassium Iodide	40.0 cc.
Three times normal Potassium Chlorate	53.3 cc.
Water	266.7 cc.
	400.0 cc.

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2\,S_2\,O_3$ used in each titration.	Per cent. of Iodine liberated.
10	20	2.8	7.0
20	20	5.0	12.5
40	20	8.25	20.6
60	20	10.6	26.5
85	20	13.5	33.8
110	20	15.4	38.5
150	20	17.35	43.4
180	20	19.25	48.1
210	20	20.25	50.6
230	20	21.4	53.5
290	20	21.85	54.6
440	20	24.2	60.5
510	20	24.75	61.9
590	20	25.6	64.0
830	20	27.4	68.5
900	20	27.8	69.5
1320	20	31.3	78.3

[1] Curve D, Figure 1.

II. Potassium iodide enters in an excess, both the hydrochloric acid and potassium chlorate remaining constant and tenth normal.

(1) Series in which the K I is *doubled*,[1]—

$$KClO_3 + 6\ HCl + 6\ KI + 6\ KI\ \text{Excess.}$$

A sample of 400 cc. was prepared as follows:

Normal Hydrochloric Acid	40.0 cc.
Normal Potassium Iodide	80.0 cc.
Three times normal Potassium Chlorate	13.3 cc.
Water	266.7 cc.
	400.0 cc.

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2S_2O_3$ used in each titration.	Per cent. of Iodine liberated.
15	20	2.4	6.0
30	20	4.7	11.8
50	20	6.35	15.9
85	20	9.65	24.1
110	20	11.45	28.6
160	20	13.85	34.6
230	20	16.7	41.8
315	20	18.55	46.4
430	20	19.9	49.8
530	20	21.4	53.5
640	20	22.9	57.3
760	20	23.65	59.1
1360	20	27.2	68.0

[1] Curve B, Figure 2.

(2) Series in which K I is *tripled*,[1]—

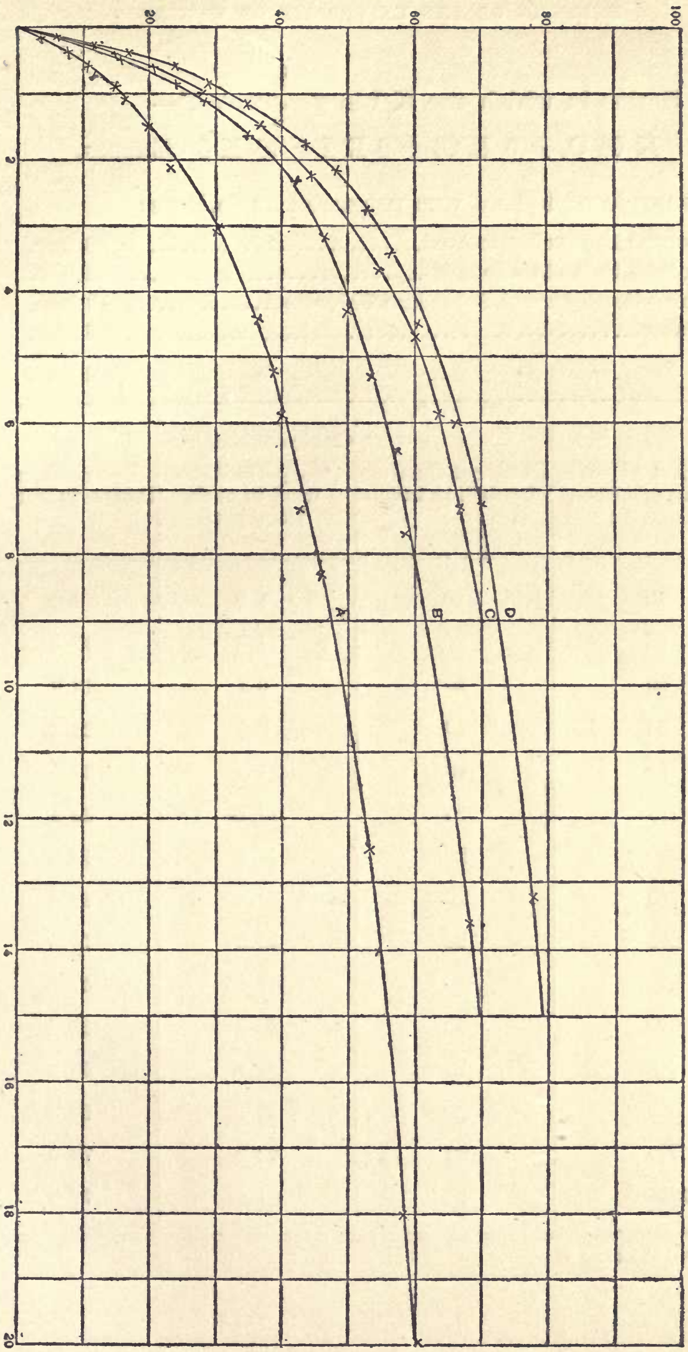
$$KClO_3 + 6\,HCl + 6\,KI + 12\,KI \text{ Excess.}$$

A sample of 400 cc. was made up as follows:

Normal Hydrochloric Acid	40.0 cc.
Normal Potassium Iodide	120.0 cc.
Three times normal Potassium chlorate	13.3 cc.
Water	226.7 cc.
	400.0 cc.

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2S_2O_3$ used in each titration.	Per cent. of Iodine liberated.
10	20	1.8	4.5
20	20	3.25	8.1
40	20	5.9	14.8
65	20	8.25	20.6
100	20	11.05	27.6
150	20	14.6	36.5
225	20	17.8	44.5
370	20	21.7	54.3
470	20	24.0	60.0
585	20	25.35	63.4
720	20	26.65	66.6

[1] Curve C, Figure 2.



II

(3) Series in which the K I is *quadrupled*,[1]—

$$KClO_3 + 6\ HCl + 6\ KI + 18\ KI\ \text{Excess.}$$

A sample of 400 cc. was prepared as follows:

Normal Hydrochloric Acid	40.0 cc.
Normal Potassium Iodide	160.0 cc.
Three times normal Potassium Chlorate	13.3 cc.
Water	186.7 cc.
	400.0 cc.

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2S_2O_3$ used in each titration.	Per cent. of Iodine liberated.
10	20	1.9	4.8
25	20	4.6	11.5
40	20	6.7	16.8
60	20	9.5	23.8
85	20	11.5	28.8
115	20	13.75	34.4
150	20	17.1	42.8
175	20	17.4	43.5
215	20	18.3	45.8
275	20	21.15	52.9
340	20	22.6	56.5
450	20	24.2	60.5
600	20	26.3	65.8
720	20	28.0	70.0
1320	20	31.0	77.5

[1] Curve D, Figure 2.

III. Hydrochloric acid enters in an excess, both the other components remaining constant and tenth normal.

(1) Series in which the original amount of H Cl is *doubled,*[1]—

$$KClO_3 + 6\,HCl + 6\,KI + 6\,HCl \text{ Excess.}$$

A sample of 400 cc. was prepared as follows:

Normal Hydrochloric Acid	80.0 cc.
Normal Potassium Iodide	40.0 cc.
Three times normal Potassium Chlorate	13.3 cc.
Water	266.7 cc.
	400.0 cc.

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2S_2O_3$ used in each titration.	Per cent. of Iodine liberated.
17	20	4.3	10.8
30	20	7.25	18.1
50	20	10.45	26.1
70	20	12.7	31.8
105	20	16.2	40.5
105	20 (CS_2)	16.35	40.9
150	20	18.95	47.4
220	20	22.3	57.5
300	20	24.85	62.1
450	20	27.55	68.9
720	20	30.95	77.4

[1] Curve B, Figure 3.

(2) Series in which the original amount of HC is *tripled,*[1]—

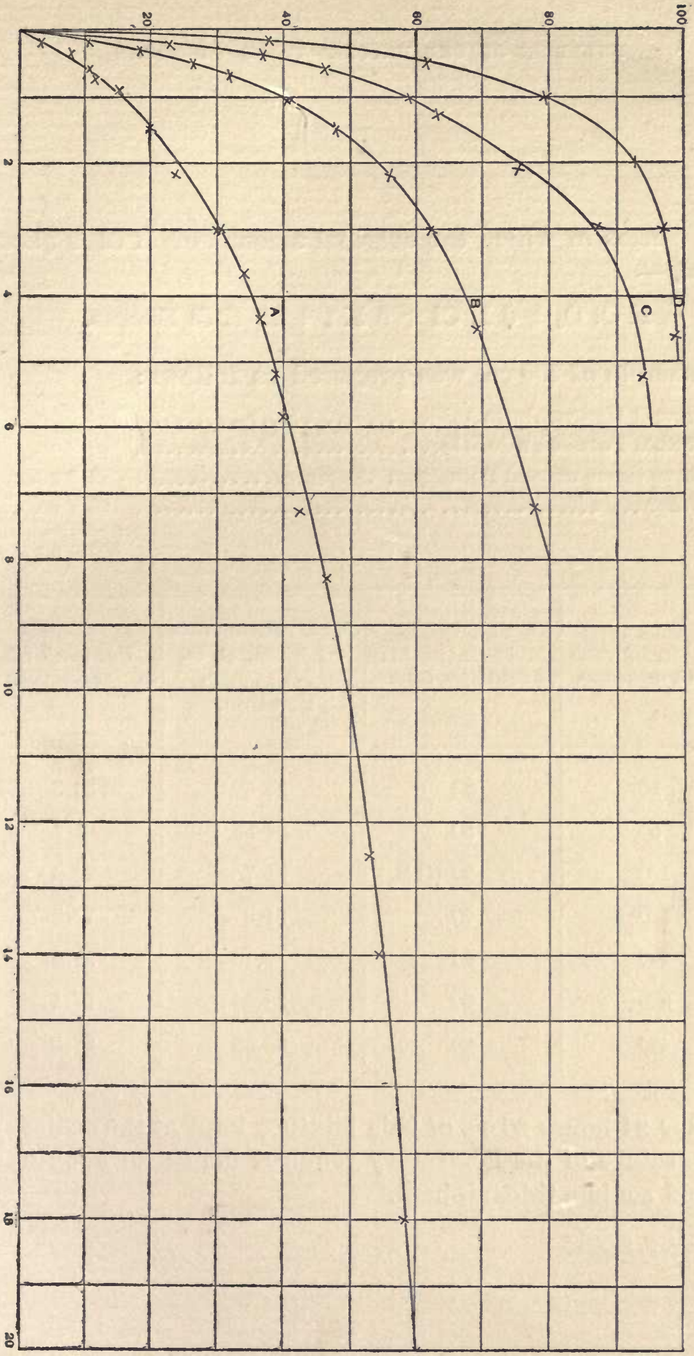
$$K\,Cl\,O_3 + 6\,H\,Cl + 6\,K\,I + 12\,H\,Cl \text{ Excess.}$$

A sample of 400 cc. was prepared as follows:

Normal Hydrochloric Acid	120.0 cc.
Normal Potassium Iodide	40.0 cc.
Three times normal Potassium Chlorate	12.3 cc.
Water	226.7 cc.
	400.0 cc.

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2S_2O_3$ used in each titration.	Per cent. of Iodine liberated.
10	20	4.6	11.5
20	20	9.05	22.6
40	20	14.75	36.9
60	20	18.75	46.4
100	20	23.6	59.0
130	20	25.35	63.4
210	20	30.1	75.3
295	20	34.95	87.4
525	20	37.5	93.8

[1] Curve C, Figure 3.



III

(3) Series in which the original amount of H Cl is *quadrupled,*[1]—

$$K\,Cl\,O_3 + 6\,H\,Cl + 6\,K\,I + 18\,H\,Cl \text{ Excess.}$$

A sample of 400 cc. was prepared as follows:

Normal Hydrochloric Acid	160.0 cc.
Normal Potassium Iodide	40.0 cc.
Three times normal Potassium Chlorate	13.3 cc.
Water	186.7 cc.
	400.0 cc.

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2S_2O_3$ used in each titration.	Per cent. of Iodine liberated.
20	20	15.3	38.3
50	20	24.55	61.4
100	20 (CS_2)	31.7	79.3
100	20	31.8	79.5
200	20	37.15	92.9
300	20	38.85	97.1
460	20	39.55	98.9

After 24 hours 20 cc. of this mixture kept at the ordinary temperature of the laboratory required 0.5 cc. of twentieth normal sodium thiosulphate.

[1] Curve D, Figure 3.

SECTION C.

This section embraces a series of experiments in which excesses of both the hydrochloric acid and potassium iodide enter, the amount of potassium chlorate remaining constant. The results obtained have a direct bearing upon analytical methods as these are the conditions under which chlorates are estimated.

(1) Series in which *both* the H Cl and K I are *doubled*, the K Cl O_3 remaining constant and tenth normal,[1]—

$$K\,Cl\,O_3 + 6\,KI + 6\,H\,Cl + \overbrace{6\,H\,Cl + 6\,K\,I}^{\text{Excess}}.$$

A sample of 400 cc. was made up as follows:

Normal Hydrochloric Acid	80.0 cc.
Normal Potassium Iodide	80.0 cc.
Three times normal Potassium Chlorate	13.3 cc.
Water	226.7 cc.
	400.0 cc.

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2\,S_2\,O_3$ used in each titration.	Per cent. of Iodine liberated.
10	20	3.75	9.4
35	20	11.35	28.4
60	20	16.5	41.3
100	20	21.3	53.3
170	20	25.75	64.4
280	20	30.4	76.0
415	20	33.6	84.0

[1] Curve A, Figure 4.

(2) Series in which *both* the H Cl and K I are *tripled*,—

$$K\,Cl\,O_3 + 6\,H\,Cl + 6\,K\,I + \overbrace{12\,K\,I + 12\,H\,Cl}^{\text{Excess.}}$$

A sample of 200 cc. was prepared as follows:

Normal Hydrochloric Acid	60.0 cc.
Normal Potassium Iodide	60.0 cc.
Three times normal Potassium Chlorate	6.7 cc.
Water	73.3 cc.
	200.0 cc.

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2\,S_2\,O_3$ used in each titration.	Per cent. of Iodine liberated.
5	10	2.6	13.0
10	10	5.05	25.3
20	10	8.75	43.8
35	10	12.0	60.0
50	10	14.15	70.8
70	10	16.25	81.3
95	10	17.85	89.3
160	10	19.8	99.0

[1] Curve B, Figure 4.

(3) Series in which *both* the H Cl and K I are *quadrupled*,—

$$KClO_3 + 6\,HCl + 6\,KI + \overbrace{18\,HCl + 18\,KI}^{\text{Excess}}.$$

A sample of 200 cc. was prepared thus:

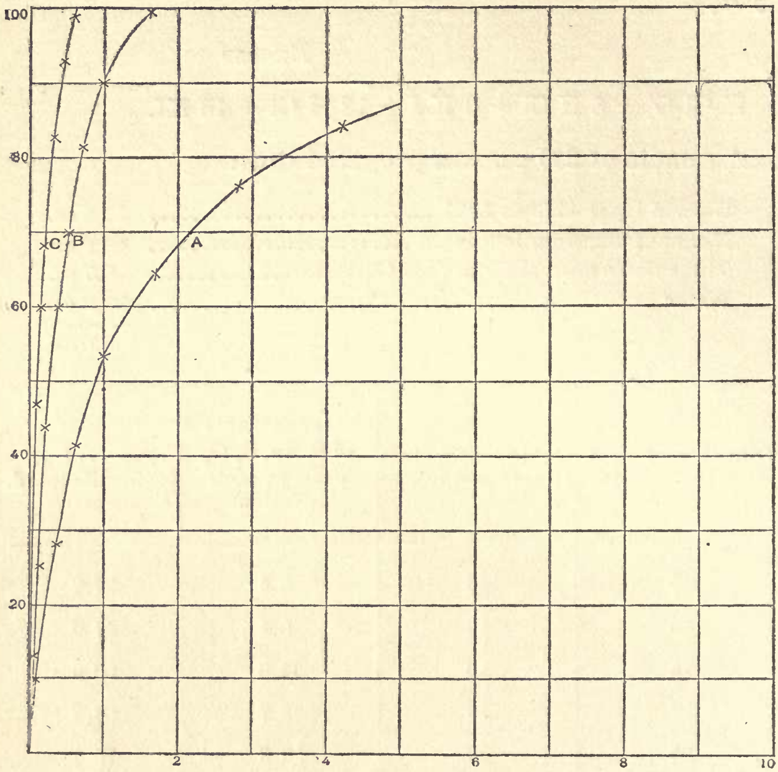
Normal Hydrochloric Acid	80.0 cc.
Normal Potassium Iodide	80.0 cc.
Three times normal Potassium Chlorate	6.7 cc.
Water	33.3 cc.
	200.0 cc.

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2S_2O_3$ used in each titration.	Per cent. of Iodide liberated.
5	10	5.4	27.0
10	10	9.4	47.0
15	10	12.0	60.0
20	10	13.7	68.5
25	10	15.3	76.5
30	10	16.5	82.5
35	10	17.3	86.5
45	10	18.6	93.0
55	10	19.75	98.8
60	10	19.95	99.8
80	10	19.9	99.5
105	10	20.1	100.5

It is to be observed here that the entire amount of iodine is liberated in an hour.

[1] Curve C, Figure 4.

IV.



(4) Series in which the K I is *doubled* and the H Cl *sextupled.*

$$KClO_3 + 6KI + 6HCl + \overbrace{6KI + 30HCl}^{\text{Excess.}}$$

A sample of 200 cc. was made up as follows:

Normal Hydrochloric Acid	120.0 cc.
Normal Potassium Iodide	40.0 cc.
Three times normal Potassium Chlorate	6.7 cc.
Water	33.3 cc.
	200.0 cc.

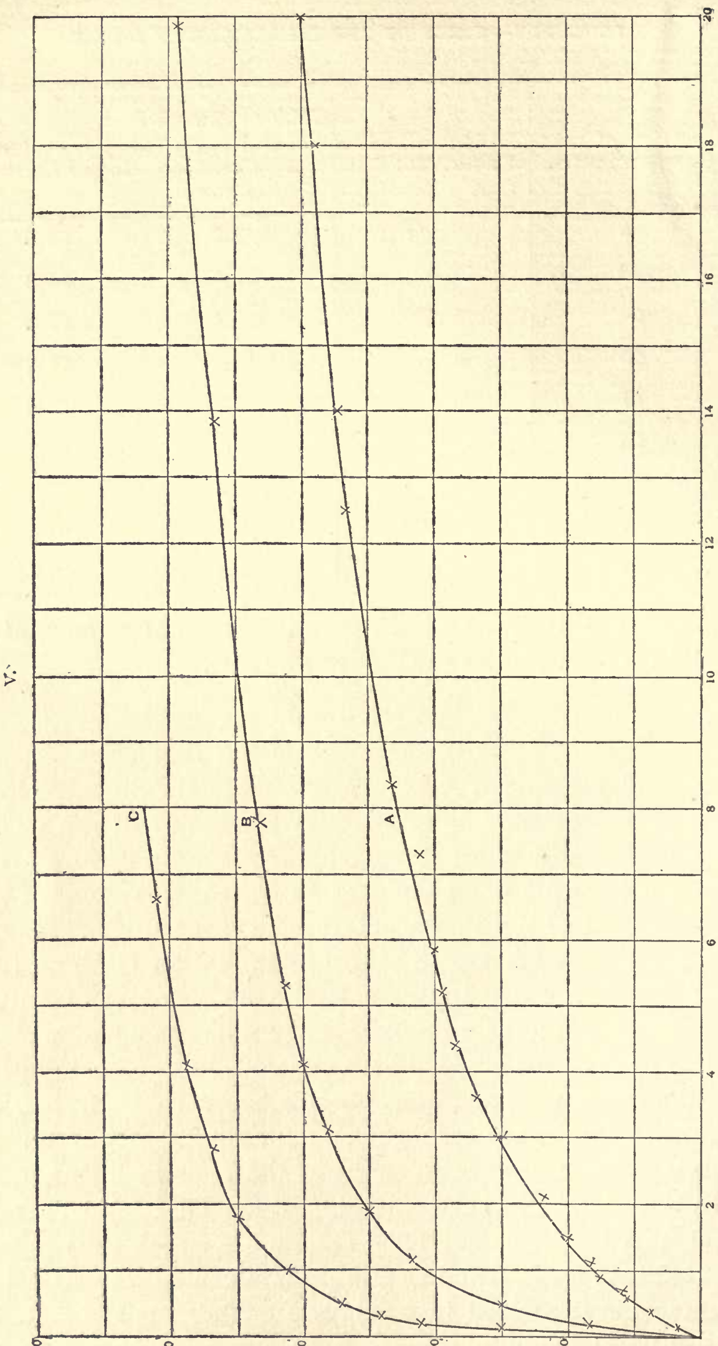
Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2S_2O_3$ used in each titration.	Per cent. of Iodine liberated.
5	10 (CS_2)	7.3	36.5
10	10	11.6	58.0
20	10 (CS_2)	15.4	77.0
20	10	15.45	77.3
31	10	17.65	88.3
35	10 (CS_2)	18.1	90.5
45	10	19.0	95.0
60	10 (CS_2)	19.9	99.5
85	10	19.9	99.5

Here too it is to be noticed that the entire amount of iodine is liberated at the end of an hour.

SECTION D.

Effect of Concentration on the Speed.

A comparison of the results in section B with those in A shows that there is an increase in the speed of the iodine liberation as one of the components enters in an excess; i. e., there is an increase in speed when *one* of the components exists in the mixture in a more concentrated form than the others. The results in section C show that there is a greater increase in the speed of the reaction when *both* the hydrochloric acid and potassium iodide enter in an excess. One would also expect an increase in speed as the component solutions became more concentrated, although none of the components entered in an excess. A mixture containing equivalents of the salts as fifth normal solutions, and another containing them as two-fifths normal were investigated. The results are graphically represented by curves B and C, Figure 5. The curve marked A represents the speed in a mixture containing the salts as tenth normal solutions.


V.
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20

(1) Series containing equivalents of the components as *fifth* normal solutions,[1]—

$$KClO_3 + 6KI + 6HCl.$$

A sample of 200 cc. was made up as follows:

Normal Hydrochloric Acid	40.0 cc.
Normal Potassium Iodide	40.0 cc.
Three times normal Potassium Chlorate	13.3 cc.
Water	106.7 cc.
	200.0 cc.

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2S_2O_3$ used in each titration.	Per cent. of Iodine liberated
10	10	4.45	11.1
20	10	6.7	16.8
50	10	11.95	29.9
115	10	17.3	43.3
190	10	20.1	50.3
310	10	22.5	56.3
410	10	23.9	59.8
530	10	25.15	62.9
780	10	26.65	66.6
1380	10	29.2	73.0
1980	10	30.4	76.0

[1] Curve B, Figure 5.

(2) Series containing equivalents of the components as *two-fifth* normal solutions,[1]—

A sample of 100 cc. was made up as follows:

Normal Hydrochloric Acid	40.0 cc.
Normal Potassium Iodide	40.0 cc.
Three times normal Potassium Chlorate	13.3 cc.
Water	6.7 cc.
	100.0 cc.

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2S_2O_3$ used in each titration.	Per cent. of Iodine liberated.
10	10	24.25	30.3
20	10	33.7	42.1
30	10	38.4	48.0
50	10	43.3	54.1
100	10	50.55	63.2
180	10	55.6	69.5
280	10	58.7	73.4
410	10	61.75	77.2
660	10	65.0	81.25

[1] Curve C, Figure 5.

SECTION E.

Acceleration of Speed by Other Acids.

The presence of an excess of hydrochloric acid accelerates the reaction. Will the presence of other acids have a similar influence, and if so what is their comparative influence on the speed of the reaction? Various acids, organic and inorganic, were tested.

Normal solutions of the following acids were prepared,—hydrobromic, nitric, sulphuric, boric, formic, acetic, propionic, butyric, tartaric, malic, lactic, succinic, and oxalic.

A mixture containing equivalents of the components as *fifth* normal solutions served as a basis throughout the investigations. The following is a general sample mixture of 200 cc.—

Normal Hydrochloric Acid	40.0 cc.
Normal Potassium Iodide	40.0 cc.
Three times normal Potassium Chlorate	13.3 cc.
Normal acid used as accelerator	20.0 cc.
Water	86.7 cc.
	200.0 cc.

It was found that none of the organic acids mentioned increased the speed of the reaction. On the contrary they all slightly retarded the liberation of iodine. [Boric acid also shows a slight retardation of the speed.] This is easily accounted for by the fact that some of the acids are oxidized by potassium chlorate. It is also possible that some of the halogens present go to form substitution products of the acid.

The results obtained by using hydrobromic, hydrochloric, nitric, and sulphuric acids respectively as accelerators are graphically represented in figure 6. Curve A represents the speed when no accelerating acid is present.

(1) Hydrobromic acid is the accelerator.[1]

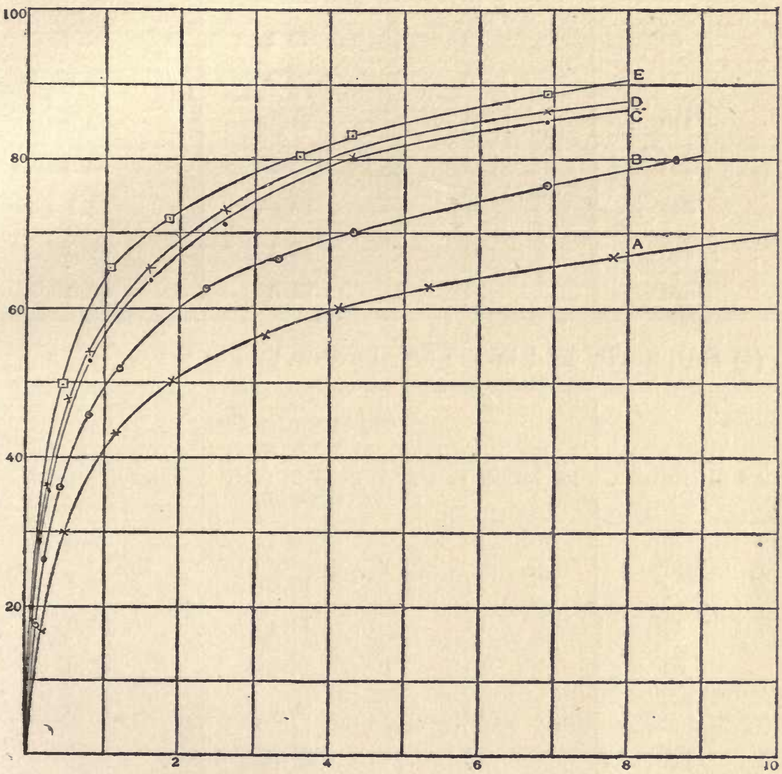
Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2 S_2 O_3$ used in each titration	Per cent. of Iodine liberated.
10	10	8.0	20.0
20	10	12.6	31.5
50	10	19.6	49.0
110	10	26.1	65.3
185	10	28.9	72.3
360	10	32.1	80.3
430	10	33.15	82.9
690	10	35.3	88.3

(2) Hydrochloric acid serves as the accelerator.[2]

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2 S_2 O_3$ used in each titration.	Per cent. of Iodine liberated.
10	10	7.2	18.0
20	10	11.5	28.8
30	10	14.4	36.0
55	10	19.1	47.8
80	10	21.6	54.0
160	10	26.1	65.3
260	10	29.15	72.9
430	10	32.15	80.4
690	10	34.55	86.4

[1] Curve E, Figure 6. [2] Curve D, Figure 6.

VI.



(3) Nitric acid is the accelerator.[1]

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2S_2O_3$ used in each titration.	Per cent. of Iodine liberated.
10	10	7.2	18.0
20	10	11.4	28.5
30	10	14.1	35.3
55	10	18.6	46.5
110	10	21.15	52.9
185	10	25.45	63.6
360	10	28.45	71.1
430	10	32.1	80.3
690	10	34.0	85.0

(4) Sulphuric acid is the accelerator.[2]

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2S_2O_3$ used in each titration.	Per cent. of Iodine liberated.
10	10	6.1	15.3
25	10	10.55	26.4
45	10	14.4	36.0
80	10	18.25	45.6
120	10	20.8	52.0
260	10	25.2	63.0
330	10	26.5	66.3
360	10	26.65	66.6
430	10	28.3	70.8
690	10	30.5	76.3
840	10	32.0	80.0

[1] Curve C, Figure 6.

[2] Curve B, Figure 6.

(5) Boric acid was also investigated. A comparison of the following results with series (1), section D, shows that the speed of iodine liberation is very slightly retarded instead of accelerated by the presence of this acid.

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2\,S_2\,O_3$ used in each titration.	Per cent. of Iodine liberated.
10	10	3.65	9.1
20	10	6.4	16.0
25	10	7.4	18.5
50	10	11·1	27.8
80	10	14.7	36.8
200	10	19.35	48.4
400	10	23.6	59.0
740	10	25.85	64.6

(6) Ten normal organic acids were also investigated. With the exception of formic acid, the results from these acids vary but slightly, so that to give any one series will be sufficient. A comparison with series (1), section D, shows a slight retardation in the speed of iodine liberation.

Duration of reaction in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2 S_2 O_3$ used in each titration.	Per cent. of Iodine liberated.
10	10	3.7	9.3
25	10	7.6	19.0
45	10	10.9	27.3
80	10	14.3	35.8
120	10	16.5	41.3
330	10	22.05	55.1
840	10	25.6	64.0

(7) Formic acid being a good reducing agent retards the speed of iodine liberation to a remarkable degree, as the following results show:

Duration of reac- in minutes.	Cubic centimeters of solution taken.	Cubic centimeters of $\frac{n}{20}$ $Na_2 S_2 O_3$ used in each titration.	Per cent. of Iodine liberated.
10	10	3.7	9.3
20	10	5.6	14.0
80	10	8.35	20.9
120	10	8.7	21.8

CONCLUSIONS.

The foregoing results lead to the following conclusions:

1. The speed of the reaction is influenced to a marked degree by the temperature, the speed increasing with the rise of temperature.

2. The presence in the mixture of an excess of one or more of the components increases the speed. The effect of an excess of potassium iodide is about the same as an equivalent excess of potassium chlorate. But a corresponding excess of acid causes a greater increase of speed.

3. Other things being equal the speed of the reaction is modified by degree of concentration of the mixtures, the speed increasing with the concentration.

4. To obtain the complete reduction of potassium chlorate by potassium iodide and hydrochloric acid in a comparatively short time, the solutions must be concentrated, there must be present quite an excess of both potassium iodide and hydrochloric acid, and the mixture must be strongly heated.

5. The presence of an excess of the ordinary inorganic acids accelerates the reaction. Assuming their respective influences as indicating their relative strengths,[1] the results on acceleration show the following order of strength: (1) hydrobromic, (2) hydrochloric, (3) nitric, and (4) sulphuric.

6. Organic acids and boric acid do not increase the speed.

This work was undertaken at the suggestion of Mr. Louis Kahlenberg, instructor in chemistry at the University of Wisconsin, and was carried out under his immediate direction. For the kindly interest he has always taken in my work I here desire to express my sincere thanks.

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[1] These acids are arranged in the same order by Ostwald, who investigated the influence of their presence on the speed of the reduction of bromic acid by hydriodic acid. Zeitsch. physik. Chem., 2. p. 135. (1888)

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