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No. 60 : THE RATE OF OXIDATION OF ARSENIUS ACID
BY CHROMIC ACID, BY RALPH E. DELURY

No. 61 : THE INDUCTION BY ARSENIUS ACID OF THE
REACTION BETWEEN CHROMIC AND HYDRIODIC ACIDS,
BY RALPH E. DELURY

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THE RATE OF OXIDATION OF ARSENIOUS ACID BY CHROMIC ACID.

BY RALPH E. DE LURY

The following measurements together with those on the rate of oxidation of iodide by chromic acid¹ constitute a necessary preliminary investigation to the study of the rates of the reactions in solutions containing arsenious acid, iodide, bichromate and sulphuric acid.²

In all of these experiments the concentration of the arsenious acid was small and the sulphuric acid and potassium bichromate concentrations relatively large, so that the results might be directly comparable with the measurements in which iodide was present. It was consequently possible to consider the concentrations of the sulphuric acid and bichromate as constant in the experiments of each table.

Method of Experimenting

A supply of distilled water and dilute solutions of potassium bichromate, sulphuric acid and arsenious acid were kept at $0^{\circ}C$ in a thermostat. The bichromate and sulphuric acid and some of the water were measured into a beaker clamped down in the bath; the arsenious acid mixed with the rest of the water necessary to make up the required total volume, was thrown into the beaker from a large test-tube, the reacting mixture violently stirred and the time noted. To stop the reaction a quantity of ammonium bicarbonate solution more than sufficient to neutralize the acid present was added to the beaker and the contents were thoroughly stirred. The residual arsenious acid was then determined by titration with volumetric iodine and arsenious acid.

Solutions Employed

The following stock solutions were prepared:

Potassium Bichromate, $K_2Cr_2O_7$, 0.1 *F*, or 0.6 *N*, prepared

¹ De Lury: *Jour. Phys. Chem.*, 7, 239 (1903).

² *Ibid.*, immediately following the present paper.

by dissolving 58.9 grams of the pure salt in 2 liters of distilled water.

Sulphuric Acid, H₂SO₄, 0.967 N, standardized gravimetrically with barium.

Arsenious Acid, As₂O₃, 0.025 F, or 0.1 N, prepared by dissolving 9.90 grams of pure "lump white arsenic" in hot water and diluting to 2 liters with distilled water; before use the solution was diluted to ten times its volume with boiled distilled water (to prevent slow oxidation by oxygen).

Iodine, approximately 0.1 N, prepared by dissolving resublimed iodine in potassium iodide solution and diluting. For titrating, this solution was diluted to ten times its volume and compared frequently with the volumetric arsenious acid solution.

Ammonium Bicarbonate, "restrainer," prepared by passing carbon dioxide into a saturated solution of commercial ammonium carbonate, diluting with its own volume of water and again saturating with carbon dioxide.

Starch Solution, "indicator," prepared frequently by dissolving a gram or two of starch in 500 cc of boiling water, cooling and allowing to settle.

Explanation of the Tables

After *Cr* and *Ac* at the head of the tables are given the amounts, expressed in 10⁻⁵ gram-formula-weights (*i. e.*, in cc of 0.01 solution) of K₂Cr₂O₇ and H₂SO₄ respectively; after *As* the amount of As₂O₃, the unit being 0.25 × 10⁻⁵ gram-formula-weights (*i. e.*, 1 cc of 0.01 N solution); after *Vol.* is given the volume of the reacting mixture in cubic centimeters.

The constant *k* is defined by the equation, $k = \frac{1}{t} \log_{10} \frac{As}{As-x}$, where *x* is the amount (expressed in cc of 0.01 N solution) of arsenious acid oxidized in *t* minutes. After *Avg.* at the end of the tables is given the average of the constants; in taking the average, bracketed numbers were omitted.

As, 9.9.

t

2

3

4

5

7

As, 9.9

t

1

2

As, 9.9

t

1

1.5

2

2.5

3

TABLE I
As, 9.94; Cr, 149; Ac, 484; Vol., 500

<i>t</i>	<i>As</i> - <i>x</i>	<i>x</i>	<i>k</i>
2	7.54	2.40	0.060
3	6.53	3.41	0.061
4	6.04	3.90	0.054
5	5.20	4.74	0.056
7	3.91	6.03	0.058
			Avg. 0.058

TABLE II
As, 9.94; Cr, 298; Ac, 484; Vol., 500

<i>t</i>	<i>As</i> - <i>x</i>	<i>x</i>	<i>k</i>
1	7.51	2.43	0.122
2	6.05	3.89	0.108
3	5.00	4.94	0.100
4	3.93	6.01	0.108
			Avg. 0.110

TABLE III
As, 9.94; Cr, 447; Ac, 484; Vol., 500

<i>t</i>	<i>As</i> - <i>x</i>	<i>x</i>	<i>k</i>
1	6.46	3.48	0.187
2	4.54	5.40	0.170
			Avg. 0.178

TABLE IV
As, 4.95; Cr, 149; Ac, 484; Vol., 500

<i>t</i>	<i>As</i> - <i>x</i>	<i>x</i>	<i>k</i>
1	4.45	0.50	(0.046)
2	3.92	1.03	0.051
3	3.44	1.51	0.053
4	3.02	1.93	0.054
5	2.72	2.23	0.052
			Avg. 0.052

TABLE V
As, 9.94; Cr, 149; Ac, 968; Vol., 500

<i>t</i>	<i>As</i> - <i>x</i>	<i>x</i>	<i>k</i>
1	6.61	3.33	(0.177)
1.5	5.56	4.38	0.168
2	4.70	5.24	0.163
2.5	3.93	6.01	0.161
3	3.17	6.77	0.166
			Avg. 0.164

TABLE VI
As, 9.94; Cr, 149; Ac, 725; Vol., 500

<i>t</i>	<i>As</i> - <i>x</i>	<i>x</i>	<i>k</i>
1	7.58	2.36	(0.118)
1.5	6.79	3.15	0.110
2	5.96	3.98	0.111
2.5	5.40	4.54	0.106
3	4.83	5.11	0.105
4	3.80	6.14	0.104
			Avg. 0.107

In the measurements of Tables I-VI the residual arsenious acid was not always titrated immediately after adding the restrainer; this introduced an error due to oxidation of arsenious acid in alkaline solution.¹ In the measurements of Tables VII-XVI the arsenious acid was titrated with iodine

¹ Kessler: Pogg. Ann., 113, 142 (1861). In an average case (Table XIV), it was found that about 0.05 cc of 0.01 *N* arsenious acid solution was oxidized in one minute after adding the restrainer.

in the ice bath immediately after stopping the reaction; to make the end-point distinct, a light and reflector and beakers coated with white enamel were used. The constants of these tables are more uniform than those of the above six tables.

TABLE VII (under CO_2)

As, 10.00; *Cr*, 20; *Ac*, 242; *Vol.*, 300

<i>t</i>	<i>As</i> - <i>x</i>	<i>x</i>	<i>k</i>
5	8.77	1.23	0.0114
10	7.67	2.33	0.0115
15	6.69	3.31	0.0116
20	5.90	4.10	0.0115
			<i>Avg.</i> 0.0115

TABLE VIII

As, 10.00; *Cr*, 20; *Ac*, 242; *Vol.*, 300

<i>t</i>	<i>As</i> - <i>x</i>	<i>x</i>	<i>k</i>
5	8.79	1.21	0.0112
10	7.66	2.34	0.0116
15	6.72	3.28	0.0115
20	6.01	3.99	0.0111
25	5.20	4.80	0.0114
30	4.75	5.25	(0.0108)
			<i>Avg.</i> 0.0114

TABLE IX

As, 20.00; *Cr*, 20; *Ac*, 242; *Vol.*, 300

<i>t</i>	<i>As</i> - <i>x</i>	<i>x</i>	<i>k</i>
5	17.32	2.68	0.0121
10	15.27	4.73	0.0117
15	13.50	6.50	0.0114
20	11.95	8.05	0.0112
			<i>Avg.</i> 0.0116

TABLE X

As, 5.00; *Cr*, 20; *Ac*, 242; *Vol.*, 300

<i>t</i>	<i>As</i> - <i>x</i>	<i>x</i>	<i>k</i>
5	4.37	0.63	0.0117
10	3.84	1.16	0.0115
15	3.32	1.68	0.0112
20	2.97	2.03	0.0113
25	2.59	2.41	0.0114
30	2.29	2.71	0.0113
			<i>Avg.</i> 0.0114

TABLE XI

As, 10.00; *Cr*, 20; *Ac*, 484; *Vol.*, 300

<i>t</i>	<i>As</i> - <i>x</i>	<i>x</i>	<i>k</i>
5	6.83	3.17	0.0332
10	4.83	5.17	0.0316
14	3.71	6.29	0.0307
			<i>Avg.</i> 0.0318

TABLE XII

As, 5.00; *Cr*, 20; *Ac*, 484; *Vol.*, 300

<i>t</i>	<i>As</i> - <i>x</i>	<i>x</i>	<i>k</i>
5	3.48	1.52	0.0315
10	2.47	2.53	0.0306
15	1.77	3.23	0.0301
20	1.30	3.70	0.0293
25	0.96	4.04	0.0287
			<i>Avg.</i> 0.0300

TABLE XIII

As, 10.00; Cr, 40; Ac, 242; Vol., 300

<i>t</i>	<i>As</i> - <i>x</i>	<i>x</i>	<i>k</i>
5	7.77	2.23	0.0219
10	6.07	3.93	0.0217
15	4.78	5.22	0.0214
			Avg. 0.0217

TABLE XIV

As, 5.00; Cr, 40; Ac, 242; Vol., 300

<i>t</i>	<i>As</i> - <i>x</i>	<i>x</i>	<i>k</i>
5	4.05	0.95	(0.0183)
10	3.24	1.76	0.0188
14	2.55	2.45	0.0209
15	2.51	2.49	0.0202
20	1.92	3.08	0.0208
25	1.76	3.24	(0.0181)
30	1.37	3.63	0.0188
			Avg. 0.0200

TABLE XV

As, 10.00; Cr, 20; Ac, 121; Vol., 300

<i>t</i>	<i>As</i> - <i>x</i>	<i>x</i>	<i>k</i>
10	9.00	1.00	0.0046
20	8.20	1.80	0.0043
22.5	7.99	2.01	0.0043
30	7.38	2.62	0.0043
			Avg. 0.0044

TABLE XVI (10° C)

As, 10.00; Cr, 20; Ac, 242; Vol., 300

<i>t</i>	<i>As</i> - <i>x</i>	<i>x</i>	<i>k</i>
10	7.15	2.85	0.0146
15	6.10	3.90	0.0146
20	5.18	4.82	0.0143
			Avg. 0.0144

The oxygen of the air, while it affects the oxidation of arsenite in alkaline solution, has no effect on the oxidation of arsenious acid by chromic acid. This is seen by comparing Tables VII and VIII. The measurements of VII were made, using solutions free from air and protecting the reacting mixture with carbon dioxide; those of VIII were made, taking no precautions to exclude air. The constants and *As*-*x* readings agree closely.

I further, satisfied myself that arsenic acid of the concentration formed in the experiments has no effect on the rate of oxidation of arsenious acid.

Discussion of the Results

Effect of the Arsenious Acid.—The fair constancy of *k* throughout the tables, more particularly in Tables VII–XVI where special precautions were taken, leads to the conclusion that the rate of oxidation of arsenious acid by chromic acid is

proportional to the first power of the concentration of the arsenious acid; conclusive proof of this is furnished by the fact that k is unaffected by changing the concentration of the arsenious acid (Tables I and IV; VII, VIII and IX; XI and XII).

Effect of the Bichromate.—Doubling the concentration of the bichromate nearly doubles the constant, or halves the time necessary for the oxidation of the same amount of arsenious acid (Tables I and II; VII, VIII and XIII; X and XIV). Trebling Cr trebles k or divides by three the time necessary for the oxidation of a fixed amount of arsenious acid (Tables I and III). The rate of oxidation of arsenious acid is thus nearly proportional to the first power of the concentration of the bichromate. This deviation from an exact first power may be attributed to incomplete dissociation of $H_2Cr_2O_7$. To account for the fall in the constant it is necessary to assume that the dissociation of the chromic acid in mixture VIII is about 7 percent greater than in XIII.¹

Effect of the Sulphuric Acid.—If the concentration of the sulphuric acid be doubled the constant is nearly trebled, or the time needed to oxidize the same amount of arsenious acid is divided by three (Tables I and V, VII, VIII and XI). The results of Table VI are in accord with this. The rate may thus be set proportional to the 1.4th or 1.5th power of the concentration of the sulphuric acid. The deviation from a sharp second power is probably due to the influence of the hydrogenion on the dissociation of the arsenious acid; it is quite possible that arsenious acid in more than one form (ions or undissociated acid) reacts with chromic acid, and the rates of these reactions involve different powers of the concentration of the hydrogenion, the resultant power being the 1.4th in the above experiments.

Effect of the Temperature.—For an increase of $10^\circ C$ in the temperature the constant is increased from 0.0114 to 0.0144 (Tables VIII and XVI); that is, the rate is increased only 26 percent, a very low temperature effect indeed.

¹ See also Jour. Phys. Chem., 7, 248 (1903).

The experimental results of this investigation are summarized in Table XVII. K is defined by the equation (*Vol.* 300 cc.),

$$\frac{dx}{dt} = K(As - x) \cdot Cr^{0.9} \cdot Ac^{1.4},$$

and hence

$$K = \frac{2.30 k}{Cr^{0.9} \cdot Ac^{1.4}} \cdot \left\{ \frac{Vol}{300} \right\}^{2.3}.$$

It will be seen that the value of K is fairly constant throughout.

TABLE XVII

Table	<i>As</i>	<i>Cr</i>	<i>Ac</i>	<i>Vol.</i>	<i>k</i>	$K \times 10^6$
I	9.94	149	484	500	0.058	84
II	9.94	298	484	500	0.110	85
III	9.94	447	484	500	0.178	95
IV	4.95	149	484	500	0.052	75
V	9.94	149	968	500	0.164	89
VI	9.94	149	726	500	0.107	87
VII	10.00	20	242	300	0.0115	82
VIII	10.00	20	242	300	0.0114	82
IX	20.00	20	242	300	0.0116	83
X	5.00	20	242	300	0.0114	82
XI	10.00	20	484	300	0.0318	86
XII	5.00	20	484	300	0.0300	81
XIII	10.00	40	242	300	0.0217	83
XIV	5.00	40	242	300	0.0200	77
XV	5.00	20	121	300	0.0044	83

Summary

The rate of oxidation of arsenious acid (dilute solutions) by bichromate and sulphuric acid, is proportional to the first power of the concentration of the arsenious acid, the 0.9th power of the concentration of the bichromate and the 1.4th power of the concentration of the sulphuric acid, that is,

$$\frac{dx}{dt} = K(As - x) \cdot Cr^{0.9} \cdot Ac^{1.4}.$$

The effect of temperature on this reaction is unusually small; for an increase of 10° C the rate is increased only 26 percent.

*University of Toronto,
May, 1905*

THE INDUCTION BY ARSENIOS ACID OF THE
REACTION BETWEEN CHROMIC AND
HYDRIODIC ACIDS

BY RALPH E. DE LURY

It has long been known that the process of oxidation in solution can often be hastened by the presence of a small quantity of some easily oxidizable substance. This phenomenon is called *induced oxidation*: the name *acceptor* is given to the substance whose oxidation is accelerated and the reagent causing the acceleration is called the *inductor*. Ferrous salts, arsenious acid and nitric oxide act as inductors and iodide as acceptor for the oxygen of chromic acid.

About the middle of the last century many cases of induced oxidation, occurring chiefly in the development of methods of analysis, were noted and classified by Schönbein, Kessler and others. By selecting various combinations of reducing and oxidizing agents the number of similar cases might be multiplied indefinitely. Many of these cases have been studied qualitatively and to a certain degree quantitatively, and the attempts to explain the results of these investigations have led to the development of the *peroxide theory* so ably championed by Manchot.¹

The peroxide theory is based on a considerable amount of qualitative and some quantitative data, and on the fact that some peroxides are known to be formed in the process of oxidation, such as hydrogen peroxide and benzoyl hydroperoxide: these peroxides may be regarded as the primary products of the oxidation of hydrogen and benzaldehyde respectively.

However, if a *non-isolable* peroxide, regarded as the cause of induced oxidation, be formed, its formation can be ascertained only by a careful study of the rates of all the reactions involved, since it is as an explanation of these rates

¹ Lieb. Ann., 325, 95 (1902).

that the peroxide theory is advanced. This obvious method of attacking the problem has been neglected, no doubt on account of the difficulties of analysis which such a method in general presents; hence the quantitative investigation of such cases has been chiefly confined to the measurement of the ratio of the amounts of inductor and acceptor oxidized when the reaction is complete.¹ Such a method will often give the oxidizing value of the intermediate product but the results are not reliable or sufficient.

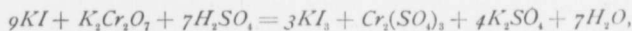
The only case of which I am aware to which the method of studying all the rates involved has been applied as yet, is the reactions in solutions containing chromic acid, iodide and ferrous salt² investigated by Miss C. C. Benson, and curiously enough the results are not in accord with the peroxide theory.

In the present paper I communicate the results of measurements of the rates of the reactions in solutions containing chromic acid, iodide and arsenious acid and am able to show that the assumption of the formation of a peroxide explains the induction in this case. The rates of oxidation of iodide³ and of arsenious acid⁴ by chromic acid have already been studied by myself.

Plan of the Investigation

In solutions containing potassium iodide, arsenious acid, potassium bichromate and sulphuric acid the following reactions may occur:

A. Oxidation of the iodide by chromic acid,



¹ Manchot: loc. cit.; Schilow: Zeit. phys. Chem. 42, 641 (1903).

² Jour. Phys. Chem., 7, 356 (1903).

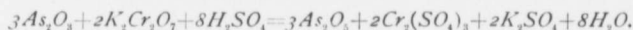
³ Ibid., 7, 239 (1903).

⁴ Ibid., 11, 47 (1907).

whose rate at $0^{\circ} C$, may be represented¹ approximately by the kinetic equation:²

$$\frac{dI_3}{dt}(c) = Ric = 1 \times 10^{-12} \cdot Cr \cdot (Ac)^2 \left[KI + 0.002(KI)^2 \right] \quad (1)$$

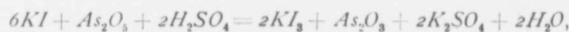
B. Oxidation of arsenious acid by chromic acid,



In the absence of potassium iodide the rate of this reaction at $0^{\circ} C$, may be represented by the equation:³

$$\frac{dAs}{dt}(c) = Rac = 83 \times 10^{-8} \cdot As \cdot (Cr)^{0.9} \cdot (Ac)^{1.4} \quad (2)$$

C. Oxidation of the iodide by arsenic acid formed in the reaction,



and the rate of this reaction at $0^{\circ} C$, may be represented⁴ thus:

$$\frac{dI_3}{dt}(a) = Ria = 4 \times 10^{-12} \cdot As \cdot KI \cdot Ac \quad (3)$$

¹ KI , Cr and Ac denote the amounts of potassium iodide, potassium bichromate and sulphuric acid respectively, expressed in 10^{-5} gram-formula-weights (i. e. in *cc.* of 0.01 *N* solution); the same unit as employed in the measurements on the rate of oxidation of iodide by chromic acid (*loc. cit.*). As and

As denote respectively the amounts of arsenious acid and arsenic acid expressed in 0.25×10^{-5} gram-formula-weights (i. e. in *cc.* of 0.01 *N* solution); this unit is selected in order to facilitate comparison between the iodine and arsenious acid readings in the Tables which follow. I_3 denotes the "free iodine" in 0.5×10^{-5} gram-formula-weights (i. e. in *cc.* of 0.01 *N* solution). The letter R denotes rate; Ric denotes the rate of oxidation of iodide by chromic acid; Rac denotes the rate of oxidation of arsenious acid by chromic acid, etc. In the subscripts ic , ac , etc. the letters i , a , c , suggest iodide (or triiodide), arsenious acid (or arsenic acid), and chromic acid respectively: the letter which goes first denoting the substance oxidized and the second letter the substance oxidizing.

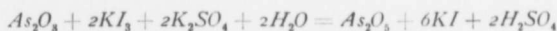
The constants are calculated for a volume of 300 *cc.*

² De Lury: *loc. cit.*

³ The paper just preceding the present paper.

⁴ Roebuck: *Jour. Phys. Chem.*, 6, 365 (1902). In concentrated solutions the indices of the power of KI and Ac are greater than 1.

D. Oxidation of the arsenious acid by the triiodide formed in the reaction,



whose rate at $0^\circ C$, is expressed by:¹

$$\frac{dAs}{dt}(i) = -\frac{dI_3}{dt}(a) = Rai = 1 \times 10^{-6} I_3 \cdot As \cdot (KI)^{-2} \cdot (Ac)^{-1} \quad (4)$$

E. Oxidation of the iodide due to the influence of the arsenious acid; the symbol Rip denotes the rate of this reaction.²

In order to simplify the study of the rate of reaction *E* the concentrations of the reagents were selected so as to reduce the rates of reactions *A*, *C* and *D* as much as possible. Of these, reaction *C* (*Ria*) gave no trouble at all since the rate constant is very small and no arsenic acid was present except that formed in reactions *B* (*Rac*) and *D* (*Rai*). The loss of I_3 by reaction *D* could not be prevented by high concentrations of *KI* and *Ac* without unduly increasing *Ric*, and in the end it was found necessary to remove the iodine as soon as it was liberated by the use of thiosulphate (see page 58).

Thus in my experiments *Ria* and *Rai* were negligibly small, and therefore,

$$\frac{dAs}{dt} = Ra = Rac + M^3 \quad (5)$$

$$\frac{dI_3}{dt} = Ri = Ric + Rip \quad (6)$$

and *Ric* being determined by blank experiments *Rip* is obtained by difference.

EXPERIMENTAL PART

It was necessary to determine the quantities of iodide and arsenious acid oxidized at any stage of the reaction. Three methods of analysis were tried.

First Method.—When a suitable interval had elapsed the

¹ Roebuck : Loc. cit.

² *p*, for peroxide in anticipation of the theory (see p. 78).

³ *M* is the modification in *Rac* due to the iodide (see p. 73).

concentration of the acid was reduced by addition of sodium bicarbonate, the iodine quickly titrated with sodium thiosulphate, excess of ammonium bicarbonate added and the residual arsenious acid titrated with iodine. This method was not successful.

Second Method.—After the reaction had proceeded for some time excess of ammonium bicarbonate was added and the arsenious acid titrated with iodine. In a duplicate experiment after the same interval, a measured quantity of 0.002 *N* thiosulphate solution, slightly in excess of the iodine present, was thrown into the reacting mixture, with violent stirring just before the ammonium bicarbonate which served as restrainer. Starch was then added and the arsenious acid and residual thiosulphate titrated with iodine, the iodine added being the sum of the arsenious acid and a *fraction* of the remaining thiosulphate. From these two measurements the arsenious acid oxidized and the iodine present could be determined if this function were known. Experiments showed that it depended on so many variables that no reliable determinations could be made, and the method was abandoned.

Third Method.—In the end a modification of Harcourt and Eßson's compensation method was found to serve, and was adopted in all the measurements of this paper. The details of the method are as follows:

Method of Making the Measurements

Distilled water and dilute solutions of potassium bichromate, sulphuric acid, potassium iodide and arsenious acid were kept at 0° C in a thermostat. The bichromate, sulphuric acid and water were mixed in a beaker coated on the outside with white enamel. In a large test-tube the iodide and arsenious acid were mixed and a little starch solution added. At a suitable time the contents of the test-tube were thrown into the beaker with violent stirring, and a stopwatch set going by pressure of the foot.

Over the beaker was clamped a 10 cc burette from which 0.01 *N* sodium thiosulphate solution was added drop by drop

as the reaction proceeded, care being taken to keep the solution in the beaker as near as possible free from both iodine and thiosulphate. A number of readings of the burette were made during each experiment, and finally after a definite interval the reaction was stopped with excess of ammonium bicarbonate, and the residual arsenious acid titrated immediately¹ with iodine.

To test the method of analysis the measurements recorded in Tables I, II and III were made. In these tables, "yellow" denotes "slight excess of thiosulphate," and "green" denotes "slight excess of iodine," that is, just enough to keep the reacting mixture bluish green with the starch present; "close" means "as near as possible free from both thiosulphate and iodine."

TABLE I

As, 10.00; KI, 9.8; Cr, 20; Ac, 484

Minutes	cc thiosulphate
5.1	1.59 yellow
5.1	1.31 close
5.1	1.09 green

TABLE II

As, 10.00; KI, 245; Cr, 20; Ac, 242

Minutes	cc thiosulphate
9.5	2.00 yellow
9.5	2.00 close
9.6	2.00 green

TABLE III

As, 10.00; KI, 98; Cr, 20; Ac, 242

cc thiosulphate	yellow	close	green
	Minutes	Minutes	Minutes
0.50	3.2	3.5	3.3
1.00	6.0	6.2	6.2
1.50	9.0	9.1	8.8
2.00	11.9	12.0	12.0

In Table I where the concentration of the iodide was low the amount of thiosulphate needed to neutralize the iodine liberated in a fixed interval, depends on the method of working. This is due to the absorption of iodine by arsenious acid, and as the rate of this reaction² is inversely proportional

¹ To prevent oxidation of the arsenite in the alkaline solution of chromate and oxygen.

² See equation (4).

to the square of the concentration of the iodide, the difference in the thiosulphate readings becomes less when the concentration of the iodide is increased and disappears when the iodide concentration is equal to (or greater than) ten times the concentration of the arsenious acid (Tables II and III). The fact that in these last two tables, the readings made when the mixture was "yellow" and "green" are the same is proof that the oxidation of thiosulphate by chromic acid¹ is negligible. In those of my measurements where the concentration of the iodide was small, I was careful to keep the reacting mixture slightly "yellow" until near the end of the interval desired; this involved an approximate knowledge of the rate at which the iodine was being liberated and in some cases necessitated the duplication of the experiments.

A number of blank experiments carried out for the purpose, showed that neither the oxygen of the air, nor the arsenic acid² and tetrathionate³ formed in the reaction, affected the rates.

Solutions Employed

In addition to the solutions, $K_2Cr_2O_7$, 0.1 *F* or 0.6 *N*; H_2SO_4 , approximately 0.1 *N*; As_2O_3 , 0.025 *F* or 0.1 *N*; ammonium bicarbonate and starch, employed in the measurements on the rate of oxidation of arsenious acid by chromic acid, a solution of potassium iodide 0.098 *F* (standardized by silver) and approximately 0.01 *N* solutions of thiosulphate and iodine (standardized by comparison with the arsenious acid), were used.

Explanation of the Tables

After *KI*, *Cr* and *Ac* at the head of the tables are given the amounts, expressed in 10^{-3} gram-formula-weights (*i. e.*, in *cc* of 0.01 *F* solution) of *KI*, $K_2Cr_2O_7$ and H_2SO_4 respectively

¹ See Bell; Jour. Phys. Chem., 7, 61 (1903).

² See equation (3) above, et seq.

³ The concentration of the tetrathionate is not large enough to cause any error due to decomposition in the alkaline solution during the short interval between adding the bicarbonate and the completion of the titration.

(the same unit as employed in the measurements of the oxidation of iodide); after As , the amount of As_2O_3 , the unit being 0.25×10^{-5} gram-formula-weights (*i. e.*, 1 cc 0.01 N solution), this unit is selected so as to facilitate comparison between the iodine and arsenious acid readings.

Under t are entered the durations of the reaction in minutes. Under h are given the amounts of thiosulphate ("hypo"), added from the small burette during the reaction expressed in cc of 0.01 N solution. Under $As-x'$ are entered the amounts of arsenious acid remaining unoxidized after t minutes, expressed in cc of 0.01 N solution; x' thus represents the amount of arsenious acid oxidized: this symbol is used only when iodide is present in the reacting mixture. The symbol x denotes the amount of arsenious acid oxidized in the absence of iodide.

Under ic in Table XXI are given the amounts of iodine (in cc of 0.01 N solution) liberated by the oxidation of iodide in the absence of arsenious acid. The experiments were carried out just like those in which arsenite was present (page 58), and the ic readings were obtained from the readings of the small thiosulphate burette. The numbers under ic in Tables IV-X and XII-XX were obtained from these by interpolation. In Table XI where the reaction was allowed to proceed until the arsenious acid was completely oxidized, the numbers under ic (*calc*) were calculated from the equation, $ic(\text{calc}) = 0.60 \frac{t}{5} \frac{20 \times 6 - 0.5(h + x')}{20 \times 6}$, thus allowing for the decrease in the concentration of the bichromate.

In all of the experiments the initial volume was as near as possible $300 - \frac{h}{2}$ cc, so that the average volume during the reaction was 300 cc. The temperature was always $0^\circ C$ except in Table XX and in one series of Table XXI where the temperature was $10^\circ C$.

The difference between the amounts of iodine liberated in the presence and absence of arsenious acid is entered under

$h-ic$. The constant, k' , is defined by the equation, $k' = \frac{1}{t} \cdot \log_{10} \frac{As}{As-x'}$. When no iodide is present k' becomes k of the tables on the oxidation of arsenious acid by chromic acid, and at the same time x' becomes x of those tables (i. e., k and x are the limiting values of k' and x' when $KI=0$).

In Tables V-IX, Ra and Rip (see page 56) represent the rates of oxidation of arsenious acid, and of iodide in the presence of arsenious acid after correcting for the direct action of chromic acid. Since the concentrations of the bichromate and sulphuric acid are so large that they may be regarded as constant, the rate, Ra , may be calculated by the equation:

$$Ra = 2.30h'.As$$

Rac is the limiting value of Ra when $KI=0$.

A rough approximation to the rate, Rip , is given by the quotient, $\frac{h-ic}{t}$; in this expression, however, the decrease in the concentration of the arsenious acid during the reaction is neglected. In the experiments of Tables V-IX this decrease is at most 25 percent, and hence the average amount of arsenite present during the interval is closely represented by $As-0.5x'$. On page 74 I show that the rate is proportional to the concentration of the arsenious acid, and have therefore employed the following expression for calculating the values of Rip :

$$Rip = \frac{h-ic}{t} \cdot \frac{As}{As-0.5x'}$$

TABLE IV
 $As, 9.94$; $KI, n, 9.8$; $Cr, 20$; $Ac, 121$; $t, 22.5$

n	h	$As-x'$	x'	ic	$h-ic$	$r = \frac{h-ic}{x'}$	k'
30	1.60	9.25	0.69	0.18	1.42	2.06	0.0014
40	1.75	9.30	0.64	0.31	1.44	2.25	0.0013
50	1.93	9.26	0.68	0.52	1.41	2.07	0.0013
60	2.03	9.33	0.61	0.70	1.33	2.18	0.0012
70	2.25	9.28	0.66	0.90	1.35	2.04	0.0013
80	2.40	9.27	0.67	1.10	1.30	1.94	0.0013

TABLE V
As, 9.94; *KI*, *n*.9.8; *Cr*, 20; *Ac*, 242; *t*, 10

<i>n</i>	<i>h</i>	<i>As</i> - <i>x'</i>	<i>ic</i>	$r = \frac{h-ic}{x'}$	<i>k'</i>	<i>Rip</i>	<i>Ra</i>	<i>Rip</i> + <i>Ra</i>
0	—	—	—	—	—	0.000	0.263	0.263
1	0.43	7.97	0.01	0.21	0.0096	0.046	0.221	0.267
2	0.70	8.32	0.02	0.42	0.0077	0.073	0.178	0.251
4	1.33	8.79	0.04	1.12	0.0053	0.137	0.122	0.259
6	1.53	8.81	0.06	1.30	0.0052	0.156	0.120	0.276
8	1.60	8.86	0.08	1.41	0.0050	0.160	0.116	0.276
10	1.74	9.00	0.10	1.75	0.0043	0.172	0.099	0.271
10	1.98	9.16	0.10	(2.41)	0.0036	0.195	0.083	0.278
12	1.80	9.07	0.14	1.91	0.0040	0.173	0.092	0.265
15	1.83	9.12	0.19	2.00	0.0037	0.170	0.085	0.255
20	1.88	9.00	0.26	(1.71)	0.0043	0.169	0.099	0.268
30	2.00	9.18	0.43	2.07	0.0035	0.163	0.081	0.244
30	2.17	9.12	0.43	2.12	0.0037	0.182	0.085	0.267
40	2.24	9.25	0.63	2.33	0.0031	0.167	0.071	0.238
50	2.58	9.29	0.95	(2.51)	0.0029	0.168	0.067	0.235
60	2.70	9.18	1.15	2.04	0.0035	0.160	0.081	0.241
70	3.02	9.25	1.45	2.27	0.0031	0.162	0.071	0.233
80	3.30	9.26	1.75	2.26	0.0031	0.160	0.071	0.231

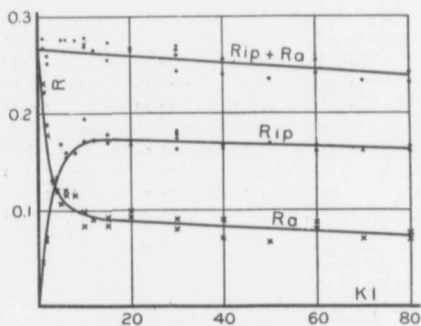


Fig. 1 (Cf. Tables V and VI)

NOTE.—In Figs. 1-4, the unit in which *KI* is represented is 9.8×10^{-3} gram-formula-weights.

TABLE VI

As, 9.94; *KI*, *n*.9.8; *Cr*, 20; *Ac*, 242; *t*, 15

<i>n</i>	<i>h</i>	<i>As</i> - <i>x'</i>	<i>ic</i>	$r = \frac{h-ic}{x'}$	<i>k'</i>	<i>Rip</i>	<i>Ra</i>	<i>Rip</i> + <i>Ra</i>
0	—	—	—	—	—	0.000	0.263	0.263
1	0.63	7.03	0.01	0.21	0.0100	0.047	0.230	0.277
2	0.95	7.48	0.02	0.38	0.0082	0.069	0.189	0.258
3	1.87	8.15	0.03	1.03	0.0057	0.134	0.131	0.265
5	2.40	8.46	0.05	1.59	0.0047	0.169	0.108	0.277
6	2.27	8.33	0.06	(1.37)	0.0051	0.160	0.117	0.277
10	2.52	8.56	0.15	1.68	0.0043	0.170	0.099	0.269
15	2.72	8.63	0.28	1.86	0.0041	0.179	0.094	0.273
20	2.78	8.63	0.39	1.82	0.0041	0.171	0.094	0.265
30	3.15	8.67	0.64	1.98	0.0040	0.178	0.092	0.270
30	3.11	8.74	0.64	2.06	0.0037	0.175	0.085	0.260
40	3.34	8.69	0.95	1.91	0.0039	0.166	0.090	0.256
60	4.00	8.73	1.66	1.93	0.0038	0.166	0.088	0.253
80	5.00	8.84	2.62	2.14	0.0033	0.166	0.076	0.242

TABLE VII

As, 19.90; *KI*, *n*.9.8; *Cr*, 20; *Ac*, 242; *t*, 10

<i>n</i>	<i>h</i>	<i>As</i> - <i>x'</i>	<i>ic</i>	$r = \frac{h-ic}{x'}$	<i>k'</i>	<i>Rip</i>	<i>Ra</i>	<i>Rip</i> + <i>Ra</i>
0	—	—	—	—	—	0.000	0.536	0.536
4	2.85	17.63	0.04	1.24	0.0053	0.296	0.243	0.539
6	3.05	17.79	0.06	1.41	0.0049	0.314	0.224	0.538
8	3.10	17.77	0.08	1.41	0.0049	0.317	0.227	0.544
10	3.20	17.83	0.10	1.50	0.0048	0.325	0.220	0.545
12	3.30	18.03	0.14	1.51	0.0043	0.330	0.198	0.534
15	3.44	18.07	0.19	1.77	0.0042	0.340	0.194	0.534
20	3.57	18.12	0.26	1.86	0.0041	0.346	0.188	0.534
30	3.76	18.26	0.43	2.05	0.0037	0.347	0.172	0.519
50	4.40	18.27	0.95	2.12	0.0037	0.359	0.172	0.531
70	4.80	18.31	1.45	2.11	0.0036	0.348	0.167	0.515

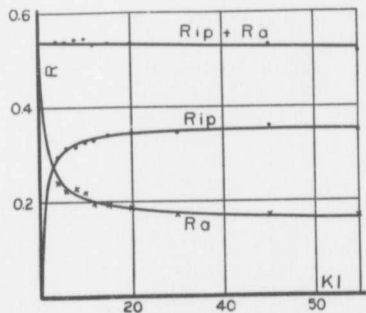


Fig. 2 (Cf. Table VII)

TABLE VIII
As, 9.94; KI, n.9.8; Cr, 40; Ac, 242; *t*, 10

<i>n</i>	<i>h</i>	<i>As - x'</i>	<i>ic</i>	$r = \frac{h - ic}{x'}$	<i>k'</i>	<i>Rip</i>	<i>Ra</i>	<i>Rip + Ra</i>
0	—	—	—	—	—	0.000	0.500	0.500
5	2.87	8.12	0.09	1.53	0.0088	0.303	0.202	0.505
10	3.10	8.28	0.18	1.76	0.0079	0.315	0.183	0.498
15	3.26	8.34	0.33	1.83	0.0076	0.316	0.176	0.492
20	3.55	8.35	0.48	1.93	0.0075	0.331	0.175	0.506
30	3.85	8.35	0.80	1.93	0.0076	0.329	0.175	0.504
50	4.82	8.40	1.80	2.00	0.0073	0.326	0.168	0.494

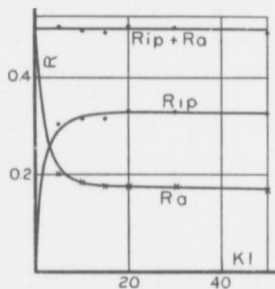


Fig. 3 (Cf. Table VIII)

TABLE IX
As, 9.94; KI, n.9.8; Cr, 20; Ac, 484; *t*, 10

<i>n</i>	<i>h</i>	<i>As - x'</i>	<i>ic</i>	$r = \frac{h - ic}{x'}$	<i>k'</i>	<i>Rip</i>	<i>Ra</i>	<i>Rip + Ra</i>
0	—	—	—	—	—	0.000	0.765	0.765
5	4.59	7.12	0.28	1.54	0.0183	0.487	0.306	0.793
10	5.06	7.32	0.56	1.72	0.0133	0.509	0.306	0.815
10	5.23	7.53	0.56	1.94	0.0121	0.525	0.279	0.804
15	5.54	7.58	0.84	2.00	0.0118	0.525	0.272	0.797
20	6.00	7.81	1.20	2.25	0.0105	0.531	0.242	0.773
20	5.67	7.57	1.20	1.89	0.0118	0.500	0.272	0.772
40	7.50	7.85	2.74	2.23	0.0103	0.526	0.237	0.763
40	7.44	7.50	2.74	1.93	0.0122	0.527	0.281	0.808
60	9.68	8.18	4.80	(2.83)	0.0085	0.531	0.196	0.727
60	9.13	7.77	4.80	1.83	0.0107	0.484	0.247	0.731

Note.—Thiosulphate solution 0.04 N was used in the measurements of this table to avoid a too great change in volume.

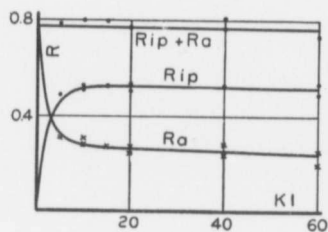


Fig. 4 (Cf. Table IX)

TABLE X

 $t = 9.5$

As	10.00	20.00	10.00	10.00	10.00
KI	245	245	490	245	245
Cr	20	20	20	40	20
Ac	242	242	242	242	484
h	2.00	3.60	2.60	3.60	6.00
$As - x'$	9.15	18.30	9.18	8.50	7.70
x'	0.85	1.70	0.82	1.50	2.30
ic	0.35	0.35	0.88	0.68	1.40
$h - ic$	1.65	3.25	1.72	2.92	4.60
$r = \frac{h - ic}{x'}$	1.94	1.91	2.10	1.95	2.00
k'	0.0040	0.0040	0.0037	0.0074	0.0119
k	0.0114	0.0116	0.0114	0.0217	0.0318
$r = \frac{k - k'}{k}$	1.9	1.9	2.1	2.0	1.7

TABLE XI

 $As, 5.00; KI, 196; Cr, 20; Ac, 484$

t	h	ic (calc.)	$h - ic$ (calc.)	t	h	ic (calc.)	$h - ic$ (calc.)
3	1.20	0.35	0.85	55	13.92	5.85	8.07
5	1.92	0.58	1.34	60	14.64	6.38	8.26
9	3.36	1.04	2.32	65	15.28	6.90	8.38
10	3.80	1.15	2.65	70	15.96	7.40	8.56
15	5.40	1.72	3.68	75	16.56	7.90	8.66
20	6.72	2.28	4.44	80	17.24	8.40	8.84
25	8.00	2.82	5.18	85	17.92	8.90	9.02
30	9.20	3.32	5.98	95	19.16	9.90	9.26
35	10.32	3.81	6.51	100	19.76	10.40	9.36
40	11.28	4.30	6.98	105	21.16	10.88	9.28
45	12.32	4.82	7.50	140	23.68	14.20	9.48
50	13.16	5.34	7.82	160	25.28	15.80	9.48

Note.—In making the iodine titrations 0.04 thiosulphate was used to avoid a too great change in volume.

Fig. 5 is plotted from the results of Table XI together with the values of x from Table XII of my paper on the oxidation of arsenious acid, and the values of x' from Table XVIII of the present paper.

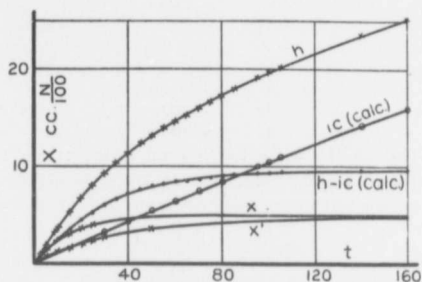


Fig. 5 (Cf. Table XI)

TABLE XII
As, 9.94; KI, 98; Cr, 20; Ac, 242

t	h	$As - x'$	x'	ic	$h - ic$	$r = \frac{h - ic}{x'}$	k'
10	1.74	9.00	0.94	0.10	1.64	1.75	0.0043
10	1.93	9.16	0.78	0.10	1.88	(2.41)	(0.0036)
15	2.52	8.56	1.38	0.15	2.37	1.72	0.0043
20	3.40	8.23	1.71	0.20	3.20	1.87	0.0041
30	4.75	7.52	2.42	0.30	4.45	1.84	0.0040

Avg. 1.80 Avg. 0.0041

TABLE XIII
As, 9.94; KI, 196; Cr, 20; Ac, 242

t	h	$As - x'$	x'	ic	$h - ic$	$r = \frac{h - ic}{x'}$	k'
5	0.98	9.48	0.46	0.14	0.84	1.83	0.0041
10	1.88	9.00	0.94	0.27	1.61	1.71	0.0043
15	2.78	8.63	1.31	0.40	2.38	1.83	0.0041
15	2.74	8.55	1.39	0.40	2.34	1.69	0.0044
20	3.66	8.23	1.71	0.54	3.12	1.82	0.0041
25	4.40	7.84	2.10	0.67	3.73	1.78	0.0041
30	5.14	7.58	2.36	0.81	4.33	1.84	0.0039

Avg. 1.80 Avg. 0.0041

TABLE XIV
As, 9.94; KI, 294; Cr, 20; Ac, 242

<i>t</i>	<i>h</i>	<i>As-x'</i>	<i>ic</i>	$r = \frac{h-ic}{x'}$	<i>k'</i>	<i>x</i>	<i>x (calc.)</i>	<i>h-ic+x'</i>
10	2.00	9.18	0.43	2.07	0.0035	—	—	—
10	2.17	9.12	0.43	2.12	0.0037	2.34	2.56	2.56
15	3.15	8.67	0.64	1.98	0.0040	3.28	3.75	3.78
15	3.11	8.74	0.64	2.08	0.0037	3.28	3.75	3.67
20	4.00	8.42	0.85	2.07	0.0036	3.99	4.76	4.67
30	5.67	7.74	1.28	2.00	0.0036	5.35	6.68	6.59
40	7.26	7.12	1.70	1.97	0.0038	6.50	8.86	8.38

Note.—The values of *x* of this table are taken from Table VIII of the paper on the oxidation of arsenious acid; *x (calc.)* is calculated as described in the foot-note on page 73.

TABLE XV
As, 5.00; KI, 196; Cr, 20; Ac, 242.

<i>t</i>	<i>h</i>	<i>As-x'</i>	<i>x'</i>	<i>ic</i>	<i>h-ic</i>	$r = \frac{h-ic}{x'}$	<i>k'</i>
10	1.15	4.57	0.43	0.27	0.88	2.05	0.0039
15	1.62	4.40	0.60	0.40	1.22	2.03	0.0037
20	2.10	4.19	0.81	0.54	1.56	1.93	0.0038
25	2.58	4.04	0.96	0.67	1.91	1.99	0.0037
30	3.04	3.85	1.15	0.81	2.23	1.94	0.0038

Avg. 1.99 Avg. 0.0038

TABLE XVI
As, 5.00; KI, 196; Cr, 40; Ac, 242

<i>t</i>	<i>h</i>	<i>As-x'</i>	<i>x'</i>	<i>ic</i>	<i>h-ic</i>	$r = \frac{h-ic}{x'}$	<i>k'</i>
5	1.10	4.69	0.31	0.24	0.86	(2.77)	(0.0056)
10	2.02	4.24	0.76	0.48	1.54	2.03	0.0072
15	2.83	3.85	1.15	0.72	2.11	1.94	0.0076
20	3.63	3.58	1.42	0.96	2.67	1.88	0.0073
30	5.09	3.05	1.95	1.44	3.65	1.87	0.0072

Avg. 1.93 Avg. 0.0073

TABLE XVII
As, 9.94; KI, 196; Cr, 40; Ac, 242

<i>t</i>	<i>h</i>	<i>As-x'</i>	<i>x'</i>	<i>ic</i>	<i>h-ic</i>	$r = \frac{h-ic}{x'}$	<i>k'</i>
5	1.84	9.14	0.80	0.25	1.59	1.99	0.0073
10	3.46	8.44	1.50	0.50	2.96	1.97	0.0071
15	4.87	7.79	2.15	0.75	4.12	1.92	0.0071

Avg. 1.95 Avg. 0.0072

TABLE XVIII

As, 5.00; KI, 196; Cr, 20; Ac, 484

<i>t</i>	<i>h</i>	<i>As-x'</i>	<i>x'</i>	<i>ic</i>	<i>h-ic</i>	$r = \frac{h-ic}{x'}$	<i>k'</i>
5	1.90	4.30	0.70	0.60	1.30	1.86	(0.0131)
10	3.59	3.80	1.20	1.20	2.39	1.99	0.0119
15	5.16	3.37	1.63	1.80	3.36	2.06	0.0114
20	6.48	2.95	2.05	2.40	4.08	1.99	0.0115

Avg. 1.98 Avg. 0.0116

TABLE XIX

As, 9.94; KI, 196; Cr, 20; Ac, 484

<i>t</i>	<i>h</i>	<i>As-x'</i>	<i>x'</i>	<i>ic</i>	<i>h-ic</i>	$r = \frac{h-ic}{x'}$	<i>k'</i>
5	3.05	8.61	1.33	0.60	2.45	1.84	(0.0125)
10	5.67	7.57	2.37	1.20	4.47	1.89	0.0118
15	8.03	6.64	3.30	1.80	6.25	1.89	0.0117

Avg. 1.87 Avg. 0.0118

TABLE XX

As, 9.94; KI, 196; Cr, 20; Ac, 242 (Temperature 10° C)

<i>t</i>	<i>h</i>	<i>As-x'</i>	<i>x'</i>	<i>ic</i>	<i>h-ic</i>	$r = \frac{h-ic}{x'}$	<i>k'</i>
10	2.55	8.90	1.04	0.35	2.20	2.1	0.0048
15	3.53	8.26	1.68	0.52	3.01	1.8	0.0054
20	4.56	7.84	2.10	0.70	3.86	1.8	0.0052
25	5.55	7.33	2.61	0.87	4.68	1.8	0.0055

Avg. 1.9 Avg. 0.0054

TABLE XXI

KI, 98; Cr, 20;

Ac, 242 KI, 196; Cr, 20; Ac, 242 KI, 294; Cr, 20; Ac, 242.

<i>ic</i>	<i>t</i>	$\frac{ic}{0^\circ C}$	$\frac{t}{0^\circ C}$	$\frac{ic}{10^\circ C}$	$\frac{t}{10^\circ C}$	<i>ic</i>	<i>t</i>	<i>ic</i>	<i>t</i>
0.20	11	0.25	9.2	0.30	10	0.48	11	2.00	46
0.28	30	0.50	18.7	0.50	15	0.81	19	2.40	57
0.83	86	1.10	42	0.85	25	1.40	31	3.20	75
1.23	120	1.20	45.5	1.10	30	1.48	35	3.84	90

KI, 392; *Cr*, 20; *Ac*, 242. *KI*, 245; *Cr*, 20; *Ac*, 242. *KI*, 686; *Cr*, 20; *Ac*, 242

<i>ic</i>	<i>t</i>	<i>ic</i>	<i>t</i>	<i>ic</i>	<i>t</i>	<i>ic</i>	<i>t</i>	<i>ic</i>	<i>t</i>	<i>ic</i>	<i>t</i>
0.24	4.2	0.87	14.5	0.31	9.5	1.33	38	0.40	2.5	2.00	13.5
0.30	5.0	1.00	17.0	0.50	14.0	1.68	47.5	0.80	5.5	3.55	26
0.58	10.0	1.21	20.2	0.67	19.0	2.00	57	1.10	7.5	3.75	27
0.80	13.2	1.20	20.7	1.02	28.5	2.64	76	1.45	10	4.10	30.4

KI, 196; *Cr*, 40; *Ac*, 242. *KI*, 196; *Cr*, 20; *Ac*, 484. *KI*, 490; *Cr*, 10; *Ac*, 242

<i>ic</i>	<i>t</i>	<i>ic</i>	<i>t</i>	<i>ic</i>	<i>t</i>
0.27	5	0.60	5	0.29	6
0.44	7.5	1.20	10	0.52	13
0.57	10	1.82	15	0.66	17
0.78	15	2.43	20	0.76	19.5
1.03	20	3.00	25	0.95	25.5
1.75	35	3.60	31	1.19	32
1.98	40	4.20	35	1.42	40
2.40	50	—	—	—	—

TABLE XXII

Table XII <i>r'</i>	Table XIII <i>r'</i>	Table XIV <i>r'</i>	Table XV <i>r'</i>	Table XVI <i>r'</i>	Table XVII <i>r'</i>	Table XVIII <i>r'</i>	Table XIX <i>r'</i>
1.7	1.7	1.5	(2.6)	(2.8)	1.7	1.4	2.4
(2.5)	1.6	2.0	1.7	2.0	1.4	2.3	1.4
1.5	1.5	1.7	1.5	1.5	—	1.5	—
1.6	1.5	1.7	—	—	—	—	—
—	1.5	1.5	—	—	—	—	—
<i>r''</i>	<i>r''</i>	<i>r''</i>	<i>r''</i>	<i>r''</i>	<i>r''</i>	<i>r''</i>	<i>r''</i>
1.9	1.9	1.9	(2.5)	(2.7)	1.9	(3.5)	2.3
2.1	1.8	2.1	1.9	2.2	1.8	(3.0)	2.1
1.8	1.8	2.1	2.0	2.1	1.6	2.4	1.9
1.9	1.8	2.0	1.8	1.9	—	2.3	—
1.7	1.8	1.9	1.7	1.8	—	—	—
—	1.7	1.8	—	—	—	—	—
—	1.6	1.6	—	—	—	—	—

TABLE XXIII

Table	IV	V	VI	VII	VII	IX
<i>As</i>	10	10	10	20	10	10
<i>KI</i>	300+	150+	150+	300+	150+	150+
<i>Cr</i>	20	20	20	20	40	20
<i>Ac</i>	121	242	242	242	242	484
<i>k</i>	0.0044	0.0114	0.0114	0.0116	0.0217	0.0318
<i>k'</i>	0.0013	0.0037	0.0038	0.0037	0.0076	0.0112
$r + 1 = \frac{k}{k'}$	3.4	3.1	3.0	3.1	2.9	2.9
$r = \frac{k - k'}{k'}$	2.4	2.1	2.0	2.1	1.9	1.9

Table	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX
<i>As</i>	10	10	10	5	5	10	5	10
<i>KI</i>	98	196	294	196	196	196	196	196
<i>Cr</i>	20	20	20	20	40	40	20	20
<i>Ac</i>	242	242	242	242	242	242	484	484
<i>k</i>	0.0114	0.0114	0.0114	0.0114	0.0200	0.0217	0.0300	0.0318
<i>k'</i>	0.0041	0.0041	0.0037	0.0038	0.0073	0.0072	0.0116	0.0118
$r + 1 = \frac{k}{k'}$	2.8	2.8	3.1	3.0	3.0	3.0	2.6	2.7
$r = \frac{k - k'}{k'}$	1.8	1.8	2.1	2.0	2.0	2.0	1.6	1.7

Note.—See also Table X.

Discussion of the Experimental Data

The measurements recorded above together with those of my previous papers on the action of chromic acid on iodide¹ and arsenious acid² constitute all the experimental data on which the theory developed in the following pages is based. In order to collect all the facts together the generalizations deduced in the last-mentioned papers are quoted in the following paragraphs along with the general conclusions drawn from the tables of the present paper.

Effect of the Concentration of the Iodide

Tables IV–IX (in each of which *t* is constant) show that increasing the concentration of the iodide causes a gradual

¹ See equation (1).

² See equation (2).

increase in the value of $h - ic$ (the iodine liberated due to the presence of the arsenious acid), and a gradual decrease in the value of x' (the arsenious acid oxidized in the presence of iodide), a maximum value of $h - ic$ and a minimum value of x' being reached when the concentration of the iodide is about fifteen times that of the arsenious acid, that is, when $KI = 15As$. Further increase in the concentration of the iodide does not appreciably affect these limiting values of $h - ic$ and x' .

When the iodide is in excess the value of the ratio, $\frac{h - ic}{x'}$, is 2.00 within the limit of the experimental error, no matter what the concentrations of the other reagents are. Thus in Tables XII-XX the average values of this ratio are, 1.80, 1.80, 2.04, 1.99, 1.93, 1.95, 1.98, 1.87 and 1.9 (at $10^\circ C$); in Table IV the values are, 2.06, 2.25, 2.07, 2.18, 2.04 and 1.94; and in Table X, 1.94, 1.91, 2.10, 1.95 and 2.00. Additional evidence is afforded by the measurements of Tables V-IX (Figs. 1-4) and the curves of Fig. 5.¹ The slight deviations in both directions, from the number 2.00 must be ascribed to experimental error, for the ratio in question is the quotient of two small numbers, each of which is the difference between two small readings of the burette, and owing to the nature of the method of analysis it usually happens that when one of these numbers (say $h - ic$) is too small the other (x') is too large.

Tables V-IX and the curves of Figs. 1-4, show that addition of potassium iodide lessens the rate of oxidation of arsenious acid by chromic acid, the retardation increasing with the concentration of the iodide up to a certain point from which on (Ra , when $KI = 0$, being equal to Rac),

$$Ra, (KI \text{ excess}) = \frac{I}{3} \cdot Rac. \quad (7)$$

Additional evidence of relation (7) is afforded by Table XXIII in which k is seen to closely equal $3 k'$.

¹ The curve, $h - ic$, approaches the line, $X = 10 = 2As$, asymptotically, and simultaneously the curve, x' , approaches the line, $X = 5 = As$.

Tables V-IX and Figs. 1-4 further show that the rate at which iodine is liberated in solutions containing arsenious and chromic acids, after correcting for the direct oxidation of iodide by chromic acid, increases with the concentration of the iodide up to a certain point from which on,

$$\begin{aligned} Rip, (KI \text{ excess}) &= 2Ra, (KI \text{ excess}) & (8) \\ &= \frac{2}{3} \cdot Rac. \end{aligned}$$

The last columns of Tables V-IX and the upper curves of Figs. 1-4, show that the sum, $Ra + Rip$, that is, the rate of reduction of chromic acid¹ after correcting for the direct action of the chromic acid on the iodide, is the same for all concentrations of iodide from zero up, or,

$$Ra + Ri - Ric = Rac \quad (9)$$

that is,

$$Ra + Rip = Rac. \quad (10)$$

Thus M of equation (5) is $- Rip$.

In the absence of arsenious acid the rate of oxidation of iodide by chromic acid is connected with the concentration of the iodide by a quadratic relation (see equation 1).

¹ On comparing the above Tables of results with those on the oxidation of arsenious acid in the absence of iodide, it will be noticed, however, that for any fixed interval of time the total oxidation is greater in the presence than in the absence of the iodide, that is, $h - ic + x'$ is greater than x for a fixed time. This is due to the fact that in the former case the concentration of the arsenious acid (on which the $h - ic$ reading depends) does not fall off so rapidly as in the latter case. If the average concentration of the arsenious acid had remained the same as it did in the experiments in which iodide was present, we would have for the value of x :

$$x(\text{calc}) = x \cdot \frac{\int_0^t x' dt}{\int_0^t x dt};$$

and as shown by Table XIV, $x(\text{calc})$ is equal to the experimentally determined value, $h - ic + x'$. For the method of computation, see Jour. Phys. Chem., 10, 423 (1906).

Effect of the Concentration of the Arsenious Acid

In the absence of iodide the rate of oxidation of arsenious acid by chromic acid is proportional to the first power of the concentration of the arsenious acid. This suggested computing the constant of the "first order" in the tables of the present paper. The constancy of k' in each of the Tables XII-XX, and more particularly the fact that changing the concentration of the arsenious acid in these tables as well as in Tables V, VI and VII, does not effect the value of k' , shows that in the presence as well as in the absence of iodide the rate of oxidation of arsenious acid by chromic acid is proportional to the first power of the concentration of the arsenious acid.

Since in the presence of excess of iodide, $h - ic = 2x'$ (see page 72), the rate Rip is twice the rate Ra , (KI_{excess}), and is therefore, like the latter, proportional to the concentration of the arsenious acid. The fact that $Rip + Ra = Rac$ for all concentrations of iodide from zero up, is also proof that Rip is proportional to the first power of the concentration of the arsenious acid.

Effect of the Concentration of the Bichromate

Comparison of Tables V and VIII, XV and XVI, XIII and XVII, shows that doubling the concentration of the bichromate almost doubles the value of k' , that is, almost doubles the rate of oxidation of arsenious acid, Ra , when iodide is present; or the rate Ra is proportional to about the 0.9th power of the concentration of the bichromate.

In the absence of iodide the same relation was found to hold; that is, Rac is proportional to the 0.9th power of the concentration of the bichromate.

Since in the presence of excess of iodide $h - ic = 2x'$, the rate Rip is twice the rate Ra , (KI_{excess}), and is therefore like the latter proportional to the same (0.9th) power of the concentration of the bichromate; and the fact that $Rip + Ra = Rac$ is also proof that the rate Rip is proportional to the 0.9th power of the concentration of the bichromate.

In the absence of arsenious acid the rate of oxidation of

iodide (*Ric*) was found to be proportional to a power of the bichromate slightly less than the first (except when very dilute solutions of bichromate were employed, when the power was the first exactly). In the above tables *ic* is scarcely doubled for a fixed interval by doubling the concentration of the bichromate.

Thus the rates *Rac Ra, Rip* and *Ric* are each proportional to a power of the concentration of the bichromate slightly less than the first.

Effect of the Concentration of the Sulphuric Acid

Doubling the concentration of the sulphuric acid nearly trebles the rates *Ra* and *Rip* in Tables V and IX, and the constants *k'* in Tables XV and XVIII, XIII and XIX. Thus the rates *Ra* and *Rip* are proportional to the 1.4th power of the concentration of the sulphuric acid.

The rate of oxidation of arsenious acid in the absence of iodide is also proportional to the 1.4th power of the concentration of the sulphuric acid. This unusual fractional power is thus common to the kinetic formulae for the rates *Rac, Ra* and *Rip*, while the rate of oxidation of iodide in the absence of arsenious acid (*Ric*) is proportional to the square of the concentration of the sulphuric acid.

Effect of the Temperature

Changing the temperature from 0° C to 10° C causes a change in the constant *k'* of 29 percent (0.0041 to 0.0053, Tables XIII and XX). Since in these tables $h - ic = 2x'$, the rate *Rip* is also increased by the same amount.

Changing the temperature has practically the same effect on the rate of oxidation of arsenious acid in the absence of iodide (*Rac*); the experiments showed that changing the temperature from 0° C to 10° C causes a change of 26 percent in the constant *k* (0.0114 to 0.0144).

Thus the rates *Rac, Ra* and *Rip* have the same unusually low temperature coefficient, *viz.*, less than 1.3.

The temperature coefficient of the rate of oxidation of iodide by chromic acid is also very low, *viz.*, 1.4.

Short Statement of the Results

The following are the general results of the experiments:

$$Rac = k.As (Cr)^{0.9}.(Ac)^{1.4} \quad (11)$$

$$Ra = k'.As (Cr)^{0.9}.(Ac)^{1.4} \quad (12)$$

$$Ric = K.(m.KI + n.(KI)^2).Cr.(Ac)^2,$$

Compare equation (1)

$$Ri - Ric = Rip = k''.As.(Cr)^{0.9}.(Ac)^{1.4} \quad (13)$$

and $Rac = Ra + Rip$.

The constants k' and k'' depend on the amount of iodide present: as the concentration of the iodide increases, k' decreases from k , for $KI = 0$, to $\frac{k}{3}$, for KI , excess; and simultaneously k'' increases from 0 to $2k'$ or $2\frac{k}{3}$.

When the iodide is in excess the ratio $\frac{h-ic}{x'}$ is equal to 2.

The rates Rac , Ra , (KI excess) and Rip , (KI excess) have the same unusually low temperature coefficient, viz., less than 1.3 (from $0^\circ C$ to $10^\circ C$); the temperature coefficient for the rate Ric is about 1.4.

THEORETICAL PART

The above results show that:

(a) The rate of reduction of chromic acid in solutions containing arsenious acid and iodide is equal to the sum of the rates of reduction of chromic acid by arsenious acid and by iodide taken separately, or, in other words, the acceleration of the rate of oxidation of iodide is just equal to the retardation in the rate of oxidation of arsenious acid.

(b) The effects of temperature and the concentrations of the various reagents are the same for the three rates:

(i) Oxidation of arsenious acid by chromic acid in the absence of iodide (Rac).

(ii) Oxidation of arsenious acid by chromic acid in the presence of excess of iodide (Ra , KI excess).

(iii) Oxidation of iodide in the presence of arsenious acid, when the iodide is in excess (Rip , KI excess).

(c) The ratio $Ra:Rip$ is independent of the concentrations of the bichromate and sulphuric acid for all concentrations of iodide.

(d) In the absence of arsenious acid the rate of oxidation of iodide is proportional to powers of the concentrations of the reagents somewhat different from those of rates (i), (ii) and (iii) of (b).

These facts suggest the theory of the formation of a primary oxide when chromic acid acts on arsenious acid, and the succeeding paragraphs will show that the above experimental results may be satisfactorily accounted for by the following assumptions.

Assumptions

(a) That arsenious acid acting on chromic acid forms slowly a primary oxide.

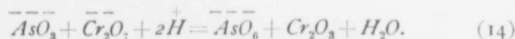
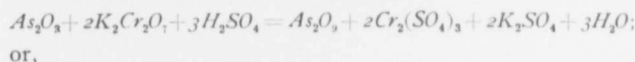
(b) That this oxide is completely and instantaneously reduced by either arsenious acid or iodide.

(c) That the fractions of the primary oxide reduced by arsenious acid and iodide respectively, in solutions containing both, depend on their relative concentrations; when the iodide is in large excess the amount of the primary oxide reduced by the arsenious acid is negligible.

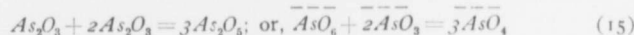
The primary oxide may be one of the following:¹

(1) A peroxide of arsenic represented by the formula, As_2O_9 , or one of its hydrates, e. g., H_3AsO_9 , the reactions being as follows:

(i) Slow formation of the peroxide,

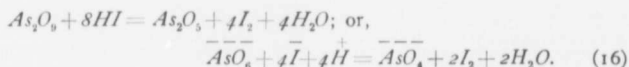


(ii) Rapid reduction by arsenious acid or iodide,

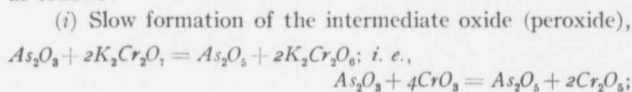


and

¹ For methods of determining the degree of oxidation of the primary oxide, see p. 83.



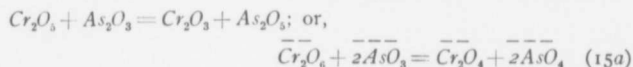
(2) An intermediate oxide¹ of chromium of the formula Cr_2O_6 , or one of its hydrates, e. g., $\text{H}_2\text{Cr}_2\text{O}_6$, the reactions being as follows:



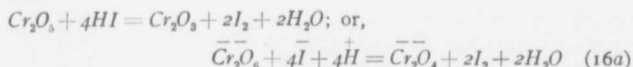
or,



(ii) Rapid reduction by arsenious acid or iodide,



and



(3) A mixed peroxide of arsenic and chromium of the same degree of oxidation as (1) and (2).

Development of the Theory

It has been found convenient to introduce the symbol Rp , for the rate of formation of the hypothetical oxide, according to equations (14) or (14a), the unit being 0.25×10^{-5} formula-weights if the oxide As_2O_6 be assumed, or 0.5×10^{-5} formula-weights if the oxide Cr_2O_6 be assumed, and the symbol Rap for the rate of oxidation of arsenious acid by peroxide, according to equations (15) and (15a). Rip has already been introduced (page 57): it may now be defined as the rate of oxidation of iodide by peroxide, as in equations (16) and (16a).

If the solution contains chromic and arsenious acids only, then for every unit of arsenious acid oxidized in the first stage

¹ Although the formula Cr_2O_6 contains less oxygen than the formula CrO_3 , I shall speak of it as a peroxide of chromium.

(formation of peroxide, equations (14) and (14a)) two more are oxidized in the second stage (reduction of peroxide, equations (15) and (15a)), the final result being the formation of three units of arsenic acid. As, by hypothesis, the second stage takes place instantaneously, the time required for the formation of this amount of arsenic acid is practically that involved in the formation of a unit of peroxide, or,

$$Rp = \frac{I}{3} \cdot Rac. \quad (17)$$

If, however, the solution contains iodide as well as arsenious acid, both will be oxidized on the reduction of the peroxide, the total quantity of iodine and arsenic acid formed in the second stage amounting to two units in all. As before, for one unit of peroxide formed and reduced three units of arsenic acid and iodine taken together are generated, and

$$Rp = \frac{I}{3} (Ra + Rip). \quad (18)$$

Whether iodide be present or not, however, for every unit of peroxide formed one unit of arsenious acid must be oxidized to arsenic acid;¹ any additional arsenic acid formed is due to the oxidation of arsenious acid by the peroxide. Thus,

$$Ra = Rp + Rap \quad (19)$$

It has been pointed out in the paragraph preceding equation (18), that two units of iodine and arsenic acid counted together are formed by the reduction of one unit of peroxide; the share of these two units, however, that falls to each, depends upon the relative concentrations of the iodide and arsenious acid. As the concentration of the iodide is increased, the reaction represented by equation (15) or (15a), falls more and more into the background until in the presence of large excess of iodide,

$$Rap, (KI \text{ excess}) = 0 \quad (20)$$

¹ If the peroxide be Cr_2O_3 , this unit of arsenic acid is formed in the first stage, equation (14a); if As_2O_3 , from the peroxide on reduction, equations (15) and (16).

So

Ralph E. De Lury

whence by equation (19),

$$Ra, (KI \text{ excess}) = Rp \quad (21)$$

and by equation (18),

$$Rip, (KI \text{ excess}) = 2Rp. \quad (22)$$

Comparison of the Theory with Results of the Experiments

By eliminating the hypothetical Rp from equations (17) to (22) the relations deduced from the assumptions of page 77, may be compared with the experimental results.

The elimination gives:

From equations (17) and (18),

$$Ra + Rip = Rac,$$

which is the same as equation (10); from equations (17) and (21),

$$Ra, (KI \text{ excess}) = \frac{1}{3} \cdot Rac,$$

which is the same as equation (7); also from equations (21) and (22),

$$Rip, (KI \text{ excess}) = 2Ra, (KI \text{ excess}) = \frac{2}{3} \cdot Rac$$

which is the same as equation (8).

That is to say, the main quantitative relations between the rates of oxidation of acceptor and inductor are in accordance with the postulates of the theory set forth on page 77. These relations are clearly shown in Fig. 6, which is in obvious agreement with Figs. 1 to 5, where the curves were plotted from the experimental data.

Further Development of the Theory

A graphic representation of the theoretical relations is given in Fig. 6, where the dotted line shows the general form of the Rip curve for increasing concentration of iodide.

Conclusions as to the relative effects of the reagents on the rates, Rap and Rip might be drawn from the form of the Rap

and R_{ip} curves before they become horizontal; unfortunately, the experimental errors incident to the method of analysis are greatest when the concentration of the iodide is small and this renders any detailed study of the curves useless.

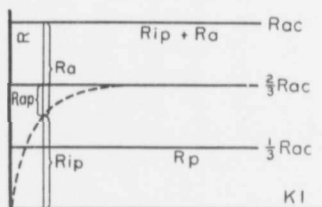


Fig. 6

However, from Tables V and VI it appears that in solutions containing *As* 10, *Cr* 20, *Ac* 242, the rates R_{ip} and R_{ap} are equal when KI is about 25. If R_{ip} were proportional to the first power of the concentration of the iodide then for $KI = 150$, $\frac{R_{ip}}{R_{ap}}$ would be 6; and if to the second power of the iodide, 36. The first is certainly far too low to be in agreement with the results while the second is not.

Again, comparison of Tables VI and VII shows that when the concentrations of both the arsenic and iodide are doubled the ratio $\frac{R_{ip}}{R_{ap}}$ is increased; or in other words the arsenious acid has less effect on the rate R_{ap} than the iodide has on the rate R_{ip} ; if R_{ip} be set proportional to the second power of the concentration of the iodide (in accordance with the conclusion reached in last paragraph), then R_{ap} must be set proportional to some lower power of the concentration of the arsenious acid—perhaps the first.

Nature of the Primary Oxide

As has been shown on page 77 the experimental results of the present paper accord equally well with either of the following assumptions:

- (1) A peroxide of arsenic.

- (2) A peroxide of chromium.
- (3) A complex peroxide of chromium and arsenic.

If one is to choose between these assumptions, additional evidence is necessary. Such evidence may possibly be obtained in the following ways:

(a) *By comparison of the powers of the reagents corresponding to the various hypotheses, with those obtained by experiment*—as suggested by Van't Hoff.

Equations (14) and (14a), corresponding to the assumptions of a peroxide of arsenic and one of chromium respectively both agree with the fact that the rate of oxidation of arsenious acid by chromic acid is proportional to the first power of the concentration of the arsenious acid and to the 0.9th power of the concentration of the bichromate (regarding the chromic acid as not being completely dissociated); and equation (14), together with the view that an ion¹ of arsenious acid reacts with chromic acid, satisfactorily accounts for the effect of the sulphuric acid concentration, while equation (14a) offers no explanation of the effect of the concentration of the acid. We thus have an argument in favor of assumption (1) or (3), and against assumption (2).

(b) *By "systematic variation of the three reagents,"* as suggested by Luther and Schilow.²

Many qualitative experiments were made substituting for chromic acid other oxidizing agents, such as, H_2O_2 , $K_2S_2O_8$, $KBrO_3$, $KClO_3$, $KClO_4$, using starch as indicator for the iodine liberated, and keeping the concentrations of the iodide and sulphuric acid sufficiently large to prevent the arsenious acid from acting on the liberated iodine. In no case was the oxidation of iodide found to be accelerated by the addition of arsenious acid. Thus we have evidence that the primary oxide is a compound of chromium (assumptions (2) and (3)).

Also when certain reducing agents are substituted for

¹ See the paper on the rate of oxidation of arsenious acid by chromic acid.

² *Zeit. phys. Chem.* **46**, 816 (1903).

arsenious acid the rate of oxidation of iodide by chromic acid is accelerated; this is noticeable in the case of some organic acids as tartaric and oxalic acids¹ and in the case of ferrous salts² in this last case, however, the acceleration cannot be ascribed to the formation of a peroxide, as Miss Benson has shown. So too, in any given case, to account for the acceleration, different types of intermediate compounds may be assumed in the absence of definite knowledge of the kinetics of the reactions, and it is in this particular that the method suggested by Luther and Schilow fails.

Summing up the evidence brought forward by the application of the above two methods, (a) and (b), we find arguments for and against the assumptions that the primary oxide is one of arsenic or one of chromium, (1) and (2), but none contrary to the view that the primary product is a complex peroxide of arsenic and chromium (3).

Determination of the Degree of Oxidation of a Hypothetical Primary Oxide

The problem of determining the degree of oxidation of an assumed primary oxide is of general interest, and some methods of doing so will now be given, using the present case in illustration.

(a) From the ratio of the quantities of acceptor and inductor oxidized in any interval (induction factor), when the concentration of the acceptor is so great that this ratio has become constant (as employed by Manchot, Luther and Schilow and others).

Let the composition of the peroxide be represented by the general formula, As_2O_{3+2r} . Then the reaction between the peroxide and arsenious acid must be written:



and that between the peroxide and the iodide,



¹ I have made some measurements on this subject, and these I hope soon to complete and publish.

² Manchot: loc. cit.; Miss C. C. Benson: loc. cit.

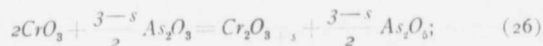
When the iodide is in excess reaction (23) is negligible, and hence for every equivalent of arsenic acid formed r equivalents of iodine are liberated, or,

$$\frac{h-ic}{x'} (KI \text{ excess}) = r, \quad (25)$$

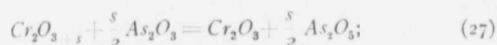
where $h-ic$ and x' are the amounts of iodide and of arsenious acid oxidized in the same time (both quantities being expressed in cc of 0.01 N solution) see page 61.

As shown on page 72, $r=2$, and hence the peroxide is As_2O_9 .

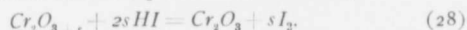
If a primary oxide of chromium be assumed the treatment is similar. Regarding CrO_3 and Cr_2O_3 as the initial and final oxides in the reduction of chromic acid, let the general formula of the peroxide be Cr_2O_{3+s} . Then for the formation of this oxide we have:



for the oxidation of arsenious acid by peroxide,



and for the reaction between peroxide and iodide,



When the iodide is in excess, reaction (27) is negligible, hence,

$$\frac{h-ic}{x'} (KI \text{ excess}) = \frac{s}{3-s}. \quad (29)$$

As shown on page 72 the value of the ratio $(h-ic):x'$, when the iodide is in excess, is 2, hence $s=2$, and the formula of the peroxide is Cr_2O_5 .

(b) From the ratio of the rates of oxidation of the inductor in the absence of the acceptor to that in the presence of excess of the acceptor.

If the peroxide be one of arsenic, As_2O_{3+n} , we have from equations (23) and (24):

$$\frac{Rac}{Ra, (KI \text{ excess})} = r + 1, \text{ or, } \frac{Rac - Ra, (KI \text{ excess})}{Ra, (KI \text{ excess})} = r. \quad (30)$$

Hence from the definitions of k and k' given on page 62.

$$\frac{k}{k'} = r + 1, \text{ or, } \frac{k - k'}{k'} = r. \quad (31)$$

Or if a peroxide of chromium, Cr_2O_{3+s} , be assumed, we have from equations (26) and (27):

$$\frac{Rac}{Ra, (KI \text{ excess})} = \frac{3}{3-s} \text{ or, } \frac{Rac - Ra, (KI \text{ excess})}{Ra, (KI \text{ excess})} = \frac{s}{3-s} \quad (32)$$

hence also,

$$\frac{k}{k'} = \frac{3}{3-s}, \text{ or, } \frac{k - k'}{k'} = \frac{s}{3-s}. \quad (33)$$

In Tables V-IX it is seen that the value of the ratio $Rac:Ra, (KI \text{ excess})$ is very close to 3; hence from equation (30), $r = 2$, and from equation (32), $s = 2$. In the summary, Table XXIII, the value of the ratio, $k:k'$ is seen to be 3; hence again r and s have the value 2 (equations (31) and (33)). Thus the formula of the peroxide must be written, As_2O_5 or Cr_2O_5 .

(c) *From the amounts of the acceptor oxidized in known intervals, assuming that the law of the oxidation of the inductor in the absence of acceptor is known*

It is generally very difficult to determine the amounts of each of two reducing agents in the presence of an oxidizing agent, and quite often impossible to find accurately the induction factor (when the reaction is over); in such cases if it is possible to make near the beginning of the reaction a few measurements of the amount of acceptor oxidized when this reagent is in excess, the degree of oxidation of the primary product may be calculated by the following methods.

The rate of oxidation of arsenious acid by chromic acid is proportional to the first power of the concentration of the arsenious acid; thus using the symbols defined on page 62, we have,

$$k = \frac{1}{t} \cdot \log_{10} \frac{As}{As-x} \quad (34)$$

and when the acceptor is present in excess,

$$k' = \frac{1}{t} \cdot \log_{10} \frac{As}{As-x'} \quad (35)$$

When the acceptor is in excess, we have, assuming the formula of the peroxide to be As_2O_{5+2r}

$$\frac{h-ic}{x'} (KI \text{ excess}) = r$$

whence, writing a for $h-ic$ to economize space,

$$x' = \frac{a}{r}$$

and we have,

$$\frac{I}{t_1} \cdot \log_{10} \frac{As}{As-a_1} = \frac{I}{t_2} \cdot \log_{10} \frac{As}{As-a_2} = \frac{I}{t_3} \cdot \log_{10} \frac{As}{As-a_3} = \dots \quad (36)$$

where $t_1, a_1; t_2, a_2; t_3, a_3;$ etc., are experimentally determined values of t and a .

(i) This equation may be solved for r , most simply by testing in turn, the numbers, 1, 2, etc.

If the rate of oxidation of the inductor had been proportional to any other power of its concentration than the first, an equation somewhat similar to (36) could be written, to be solved for r .

(ii) If it be assumed that the value of k in equation (34) be known, r can be found from the following equation (which is obtained from (31) and (33)):

$$k' = \frac{k}{r+I} = \frac{I}{t} \cdot \log_{10} \frac{As}{As-\frac{a}{r}} \quad (37)$$

by putting it in the form,

$$\begin{aligned} \frac{2.30k}{r+I} &= -\frac{I}{t} \cdot \log_e \left(1 - \frac{a}{r.As} \right) \\ &= \frac{I}{t} \left\{ \frac{a}{r.As} + \frac{I}{2} \left(\frac{a}{r.As} \right)^2 + \frac{I}{3} \left(\frac{a}{r.As} \right)^3 + \dots \right\}. \end{aligned} \quad (38)$$

If the fraction $\frac{a}{r.As}$ be very small we have as a first approximation,

$$\frac{2.30k}{r+I} = \frac{I}{t} \cdot \frac{a}{r.As} \quad (39)$$

and since $a = h - ic$ we have,

$$r = \frac{0.4343(h-ic)}{k.t.As - 0.4343(h-ic)} = r' \text{ of Table XXII.} \quad (40)$$

Using this approximation the values of r' given in Table XXII were calculated. It will be noticed that the value of r' diminishes as a (i. e., $h - ic$) increases, because the neglected terms of equation (38) become larger and larger. Hence a closer approximation is to be desired:

$$\frac{2.30k}{r+t} = \frac{t}{t} \left(\frac{a}{r.As} + \frac{t}{t} \left(\frac{a}{r.As} \right)^2 \right) \quad (41)$$

and hence,

$$r = \frac{a}{4.As} \sqrt{\frac{(a+2.As)^2 + 8.As(2.30k.t.As-a) + (a+2.As)}{2.30k.t.As-a}} = r'' \text{ of Table XXII.} \quad (42)$$

The values of r'' in Table XXII were calculated by means of formula (42).

These values do not fall off so noticeably on increasing the value of a (i. e., $h - ic$) as do the values of r' in the same table. Both r' and r'' point to the number 2 as the value of r . A slight error in k or a will cause a considerable error in the value of r'' ; this is noticeable in initial values of some of the tables.

(iii) The value of r may be found also in the following manner:

We have

$$\frac{dx'}{dt} = 2.30k'(As - x'),$$

and since $a = r.x'$, it follows that

$$\frac{da}{dt} = 2.30k'(r.As - a), \quad (43)$$

whence,

$$a = 2.30k' \int_0^a (r.As - a). dt = 2.30k'(r.As.t - \int_0^a a. dt),$$

and therefore,

$$\frac{a}{t} = 2.30k'(r.As - \int_0^a a. dt). \quad (44)$$

Now the values of $\int_0^t a \cdot dt$ can be found easily and accurately from the plotted curve, a , t , and hence the values of k' and of $r \cdot As$ can be found by means of equation (44) for any two pairs of values of a and t . Thus, we have

$$\frac{r \cdot As}{As} = \frac{h - ic}{x'} \text{ (for } t = \infty) = r^A. \quad (45)$$

If in addition the value of k of equation (34) be known, the value of r can be determined from the above calculated value of k' as in equation (31).

SUMMARY

A method of analysis, which may be of use in the study of other complicated cases of induced oxidation, is described.

Addition of potassium iodide lessens the rate of oxidation of arsenious acid by chromic acid, the retardation increasing with the concentration of the iodide up to a certain point from which on the rate of oxidation of arsenious acid is equal to one-third the rate when no iodide is present; or symbolically,

$$Ra(KI \text{ excess}) = \frac{1}{3} \cdot Rac.$$

The rate at which iodine is liberated in solutions containing arsenious acid, iodide and chromic acid, after correcting for the direct oxidation of iodide by chromic acid, in-

¹ As an example of this method the following table calculated from the data of Table XI, by methods described in Jour. Phys. Chem., 10, 423 (1906) is given.

t	$\int_0^t a \cdot dt$	$r \cdot As$
(1) 20	2.55	—
(2) 25	2.96	—
(3) 30	3.42	10.0, from (1) and (3)
(4) 35	3.83	10.4, from (2) and (4)
(5) 40	4.19	10.4, from (3) and (5)

In this table $a = h - ic$ (calc.) of Table XI. The value of As is 5.00 and hence $r = 2$ very closely.

creases with the concentration of the iodide up to a certain point from which on the rate of liberation of iodine is twice the rate of oxidation of arsenious acid (expressing both iodide and arsenious acid in equivalents), or,

$$Rip = 2Ra, (KI \text{ excess}).$$

The rate of reduction of chromic acid (after correcting for the direct action of the iodide) is the same for all concentrations of iodide from zero up, or,

$$Ra + Ri - Ric = Ra + Rip = Pac.$$

Expressing each of the three rates, Rac (rate of oxidation of arsenious acid by chromic acid in the absence of iodide), Ra (rate of oxidation of arsenious acid in the presence of iodide) and Rip (rate of liberation of iodine after correcting for the direct action of the chromic acid on iodide), in terms of the concentrations of the reagents, we have

$$Rac = k.As.(Cr)^{0.9}.(Ac)^{1.4}$$

$$Ra = k'.As.(Cr)^{0.9}.(Ac)^{1.4}$$

$$Rip = k''.As.(Cr)^{0.9}.(Ac)^{1.4}$$

where k' and k'' depend on the concentration of the iodide. When the iodide is in excess,

$$k = 3k' = \frac{3}{2}k''.$$

The effect of the temperature on the rates Rac , Ra (KI excess) and Rip , (KI excess) is the same, the coefficient being unusually small (somewhat less than 1.3).

The results may be accounted for by assuming:

(a) That arsenious acid acting on chromic acid forms slowly a primary oxide.

(b) That this oxide is completely and instantaneously reduced by either arsenious acid or iodide.

(c) That the fractions of the primary oxide reduced by arsenious acid and iodide respectively, in solutions containing both, depend on their relative concentrations: when the iodide is in large excess the amount of the primary oxide reduced by the arsenious acid is negligible.

The primary oxide may be one of the following:

(1) A peroxide of arsenic represented by the formula, As_2O_6 , or one of its hydrates, *e. g.*, H_3AsO_6 .

(2) An intermediate oxide of chromium of the formula, Cr_2O_5 , or one of its hydrates, *e. g.*, $H_2Cr_2O_6$.

(3) A complex peroxide of arsenic and chromium of the same degree of oxidation as (1) and (2).

Other evidence is in support of the view that the peroxide is one of arsenic; and still other evidence favors the assumption that the primary oxide is a compound of chromium; *the view that the primary oxide is a complex peroxide of arsenic and chromium is, however, in best accord with all the facts.*

Methods are described by which the degree of oxidation of a hypothetical primary oxide may be determined.

The above experimental work was completed in the Chemical Laboratory of the University of Toronto in May, 1905.

I wish here to express my thanks to Professor W. Lash Miller at whose suggestion this research was undertaken, for his kind advice and assistance throughout.

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