

THE RATE OF THE REACTION BETWEEN ARSE- NIUS ACID AND IODINE IN ACID SOLUTION; THE RATE OF THE REVERSE REACTION; AND THE EQUILIBRIUM BETWEEN THEM

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INTRODUCTION

The early researches on the rates at which chemical reactions take place in homogeneous systems at constant temperature, led to the enunciation of the simple law that "*the rate at any moment is proportional to the concentrations of the reacting substances at that moment.*"

$$dx/d\theta = k(A - x)(B - x)(C - x) \dots \quad \text{Eq. 1.}$$

Considerations based on the relationship between the rates of inverse chemical reactions and the composition of the system at equilibrium (Guldberg and Waage's equation) made it seem probable that this law should be modified, and that the concentration of each reagent should appear as a factor on the right of Eq. 1, *once for each molecule of that substance entering into the reaction*; and the expression

$$dx/d\theta = k(A - x)^a(B - x)^b(C - x)^c \dots \quad \text{Eq. 2.}$$

corresponding to the chemical equation for the reaction



may be regarded as the fundamental equation of Chemical Kinetics. The mathematical consequences of this equation have been developed at length for a number of cases.

It is very difficult, however, to bring much of the recent work on Chemical Kinetics into line with the requirements of Eq. 2, although a great deal of ingenuity has been expended in the attempt, and no hesitation has been shown in writing formulas for and ascribing properties to hypothetical non-

isolable "intermediate products," in order to help out the assumption of imaginary "initial reactions."

Under these circumstances, it is worth while to examine the fundamentals of the theory somewhat critically. The introduction of the indices into Eq. 2 is based on the so-called "kinetic view of chemical equilibrium," viz.: that in a system at equilibrium the two opposite reactions are still taking place, but at equal rates. According to this view the concentration function of Guldberg and Waage's equation is to be regarded as the quotient of two other concentration functions belonging to the kinetic equations of the two opposite reactions.

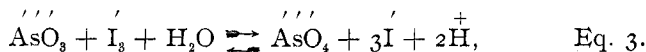
The consequences of this assumption have been subjected to a strict test in one case only,¹ viz.: the Esterification-Saponification reaction, a reaction which in every respect behaves normally; the results were in accordance with the theory of kinetic equilibrium. The present research was undertaken with a view of ascertaining whether this theory may legitimately be extended to reactions whose rates can be accounted for only by assuming the existence of hypothetical "intermediate compounds."

The reaction selected for the trial was that between arsenious acid and iodine in acid solution. These substances react to form arsenic and hydriodic acids; the reaction is reversible, and under suitable conditions of temperature and dilution proceeds at a rate convenient for measurement.

The "ordinary" chemical equation representing this reaction is



Adopting the notation of the ion theory, this equation may be written²



and the condition of equilibrium is:

¹ Zeit. phys. Chem. 22, 268 (1897).

² Nothing certain is known as to the ions in a solution of arsenious acid. See page 391.

$$\text{Const.} = \frac{a.b}{x.y^3.z^2} \quad \text{Eq. 4.}$$

(where a represents the concentration of the AsO_3 , b that of the I_3 , and so forth in the order of Eq. 3. The "concentration of the water" is constant).

This equation is in agreement with the experiments on equilibrium of Table XXXIII.

Predictions of the theory

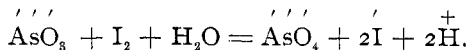
According to the theory of kinetic equilibrium, the expression $\frac{a.b}{x.y^3.z^2}$ must be regarded as the quotient of two others, for instance (i) $a.b$ and $x.y^3.z^2$, corresponding to the kinetic equations:

$$dx/d\theta = k.a.b, \text{ and } -dx/d\theta = k'.x.y^3.z^2, \quad \text{Eqs. 5, 6.}$$

Should the experiments show that the rate of oxidation of arsenious acid was proportional to the first powers of the concentrations of the AsO_3 and I_3 , the theory would require that the rate of the reverse reaction (reduction of arsenic acid by hydrogen iodide) should be in accordance with Eq. 6; and the "explanation" would be furnished by assuming that "the reactions whose rates are really measured" are those represented in Eq. 3.

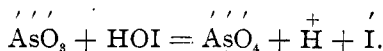
But this is obviously not the only way in which the fraction in question can be divided into two factors;¹ a number of other possibilities are enumerated in the following paragraphs.

(ii) $a.b/y$ and $1/x.y^2.z^2$; assuming the instantaneous reaction $\text{I}_3 \rightleftharpoons \text{I}_2 + \text{I}$, this may be explained by the chemical reaction:

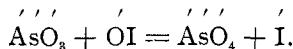


(iii) $a.b/y^2.z$, and $1/x.y.z$; assuming the instantaneous reactions $\text{I}_3 \rightleftharpoons \text{I}_2 + \text{I}$, and $\text{I}_3 + \text{OH} \rightleftharpoons \text{IOH} + 2\text{I}$, this may be explained by the chemical equation:

¹ Some of the possible factorings obviously cannot correspond to kinetic equations. To choose an extreme case, a , and $b/x.y^3.z^2$.



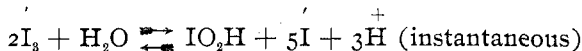
(iv) $a.b/y^2.z^2$ and $1/x.y$; adding to the assumptions of (iii) the following, viz: $\text{HOI} \rightleftharpoons \overset{+}{\text{H}} + \overset{'}{\text{OI}}$, this case may be explained by:



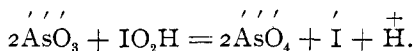
(v) Equation 4 may be changed into the form:

$$\text{Const.} = \frac{a^2.b^2}{x^2.y^6.z^4}$$

and this may be factored. For instance, into $\frac{a^2.b^2}{y^5.z^3}$ and $1/x^2.y.z$, which may be explained by the help of the reactions:



and



(iv) Finally both numerator and denominator of the fraction of Eq. 4 may be multiplied by one and the same quantity (for instance by z), and the product may be factored. Under this head would come explanations based on "catalysis by hydrogen ions," etc., etc.

After reading the preceding paragraphs, the thought suggests itself, that, no matter what relation might be found to subsist between concentrations and rates, an "explanation" would be forthcoming. The object of this research, however, was not to seek such explanations, but to ascertain whether the connection between the forms of the rate and equilibrium functions postulated by the theory, exists in reality.

PART I.

THE RATE OF OXIDATION OF ARSENIOS ACID BY IODINE IN ACID SOLUTION

EXPLANATION OF THE TABLES

Units

For the purposes of this paper, one unit of arsenious acid is defined as the quantity of arsenious acid represented by the symbol AsO_3 in centigrammes; this corresponds to 0.99 grammes of white arsenic. Similarly, one unit of arsenic acid is 1.42 grammes of H_3AsO_4 . One unit of "free iodine" is 3×1.269 grammes of I_3 ("triiodion"); it may be obtained by dissolving 2×1.269 grammes solid iodine in potassium iodide solution. One unit of "iodion" may be obtained by dissolving 3×1.66 grammes potassium iodide; and one unit of sulphuric acid (0.98 gramme H_2SO_4) is contained in 20 cc of "normal" sulphuric acid.

Representing by A, B, C, and D, the initial weights of the triiodion, arsenious acid, iodion, and acid, expressed in these units, and by x , the number of units of triiodion reduced at the time θ , the residual weights of the four constituents at this moment will be $A - x$, $B - x$, $C + x$, and $D + x$. In a solution whose initial composition is known, the quantities of all four components at any moment may, therefore, be ascertained by determining the "free iodine" by sodium thiosulphate.

The unit of volume is one litre. The unit of time is one minute.

Description of tables

At the head of each table is given the total volume of the solution in which the reaction was carried out, and also the number of units of each reagent present in that volume at the moment of mixing.

Under "Reading" is entered the number of cc of sodium thiosulphate used in the titration; this is proportional to the corresponding value of $A - x$. In the experiments of Series B,

this entry has a different meaning, which is explained on page 372.

The "constants" k_1 , k_2 , k_3 , and k_4 were calculated from the data of the tables by means of the following equations:

$$dx/d\theta = 2.30 k_1(A - x),^1$$

$$dx/d\theta = k_2(A - x)^2$$

$$dx/d\theta = k_3 V \frac{(A - x)(B - x)}{(C + x)^2 D} = k_4 \frac{(A - x)(B - x)}{(C + x)^2},$$

$$\text{whence } k_3 V/D = k_4.$$

In calculating these constants, the time of the first reading (line 2 in the tables), and not the moment of mixing, was in general taken as the starting point. The labor of computation was much shortened by the use of an exponential method, which will shortly be published.

METHOD OF CARRYING OUT THE EXPERIMENTS

The reaction was carried on in a 600 cc flask kept at 0° C by immersion in a well stirred bath of snow and water. At intervals 50 cc were pipetted into a beaker in the bath; the time was noted and the triiodion determined.

The initial composition

The stock solutions from which the reacting mixtures were made up were (I.) white arsenic dissolved in a solution of sodium bicarbonate, (II.) iodine dissolved in a solution of potassium iodide, (III.) potassium iodide solution, (IV.) dilute sulphuric acid. They were made up and standardized in the usual manner.

In calculating the initial composition, the amount of acid necessary to neutralize the soda of the arsenite solution was deducted from the total amount of acid added. Similarly with the iodine; from the potassium iodide used in making up solution (II.) was subtracted the part which united with the iodine to form triiodion, and the difference was added to the potassium iodide supplied from stock solution (III.) in calculating the

¹ In the tables of *Series B*, A in this formula was replaced by B .

initial amount of the iodion. For example, in making up the solution for the experiments of Table I., I used sodium arsenite solution 50 cc, containing $50 \times 49.4/1000$ units AsO_3 , and soda sufficient to neutralize $50 \times 0.0396 = 1.98$ units of sulphuric acid; iodine solution 5 cc, containing $5 \times 49.2/1000 = 0.246$ units triiodion, and $5 \times 17.6/1000 = 0.088$ units iodion; potassium iodide solution 50 cc, containing $50 \times 29.3/1000 = 1.47$ units iodion; sulphuric acid, 10 cc $9.43 \text{ n.acid} = 4.715$ units; water, 485 cc.

Hence the initial composition of the solution was :

AsO_3 , 2.47 units = B.

Triiodion, 0.246 unit = A.

Iodion, $1.47 + 0.088 = 1.56$ units = C.

Acid, $4.715 - 1.98 = 2.735$ units = D.

Volume, 600 cc = 0.6 unit = V.

Determination of the residual free iodine

Preliminary experiments showed that sodium thiosulphate is oxidized by acid solutions of arsenic acid, the rate of oxidation increasing with increased concentration of the thiosulphate and of the acid. As dilution, or removal of the acid (by acetates or carbonates) accelerates the rate of the reaction between arsenious acid and iodine, these obvious methods of overcoming the difficulty were excluded.

A special investigation, however, showed that if care were taken to avoid excess of thiosulphate during the titration, the error due to the oxidation could be neglected in solutions containing less than 50 grammes of H_2SO_4 per liter. I accordingly restricted¹ my measurements to solutions which were normal or less than normal with respect to the acid. The greater part of the thiosulphate solution was run in quickly, the contents of the beaker being well stirred meanwhile, and the titration was

¹ A litre of a strong solution of an alkaline carbonate readily dissolves 100 grammes of arsenious oxide; but if such a solution be acidified the greater part of the arsenic will crystallize out. This set a limit to the concentration of the arsenious acid in my experiments.

completed without excess of thiosulphate. I endeavored to determine the residual arsenious acid directly by Penot's method, after removing the triiodion by sodium thiosulphate. The end point however was very unsatisfactory (no doubt owing to the large quantity of potassium iodide present) and the attempt was given up.

In the experiments of Series B, where triiodion was in excess, the titration was begun by adding approximately normal sodium thiosulphate solution from a pipette in quantity sufficient to react with all the triiodion initially present *minus* an amount equivalent to the arsenious acid initially present. The readings were then finished with a more dilute solution from a burette. The burette readings were thus proportional to the amount of arsenious acid unoxidized, and are entered in the tables under the heading "Reading." The experimental error is comparatively large in cases of this nature, where the value of x is obtained in the form of a small difference between two large numbers.

All pipettes used were calibrated at the outset by weighing the water discharged; both in the calibration and in subsequent use 30 seconds was allowed for draining.

RESULTS OF THE EXPERIMENTS

Series A

With a view to determining the effect exercised by each component on the rate of the reaction, I carried out a set of experiments, Series A, whose results are summarized in Tables I. to VII. In all these the quantity of triiodion present initially was very much less than that of the acid, the iodion, or the arsenious acid. The concentrations of these latter, and consequently their effect on the rate remained approximately constant during the progress of the reaction, while the concentration of the triiodion fell to less than 1/10 of its initial value.

In Table I. the constancy of k_t as compared with k_2 , shows that the rate is proportional to the first power of the concentration of the triiodion.

In Table II. the initial concentrations of triiodion, potassium iodide, and acid are the same as in Table I., but that of the

TABLE I.

A, 0.246; B, 2.47; C, 1.56; D, 2.735; V, 0.6

No.	Reading	θ	A - x	$k_1 \times 10^2$	$k_4 \times 10^2$	$k_2 \times 10$
1	42.6	0.0	0.246	—	—	—
2	30.8	5.0	0.178	—	—	—
3	25.5	8.67	0.147	2.23	5.95	3.23
4	22.0	11.8	0.127	2.15	6.48	3.41
5	18.6	15.8	0.1074	2.03	5.52	3.40
6	15.35	19.7	0.0886	2.06	5.71	3.84
7	13.15	23.3	0.0759	2.02	5.68	4.14
8	11.5	26.7	0.0664	1.97	5.57	4.56
9	9.1	31.8	0.0526	1.97	5.76	5.00
10	7.33	37.2	0.0423	1.93	5.67	5.69
11	5.35	45.3	0.0309	1.89	5.67	6.63
12	2.83	60.0	0.0163	1.89	—	10.1
Average				5.7		

TABLE II.

A, 0.246; B, 4.95; C, 1.56; D, 2.735; V, 0.6

No.	Reading	θ	A - x	$k_1 \times 10^2$	$k_4 \times 10^2$
1	42.7	0.0	0.246	—	—
2	23.2	3.8	0.134	—	—
3	18.65	6.3	0.1074	3.40	5.33
4	14.35	8.67	0.0827	4.25	6.08
5	10.4	11.7	0.0599	4.40	6.40
6	8.15	14.2	0.0470	4.37	6.48
7	6.55	16.3	0.0377	4.39	6.59
8	4.4	20.8	0.0254	4.25	6.45
9	3.5	23.0	0.0202	3.86	6.55
10	1.85	30.0	0.0107	4.20	—
Average				6.4	

arsenious acid is doubled. The value of k_1 , calculated from the readings in this table, is double that of k_1 in Table I. It follows that the rate of the reaction is proportional to the first power of the concentration of the arsenious acid.

In Table III. the concentration of the iodion is approximately four times as great as in Table I., and k_1 has fallen to about one-fourteenth of its value in Table I.; that is, the rate is

TABLE III.
A, 0.246 ; B, 2.47 ; C, 5.95 ; D, 2.735 ; V, 0.6

No.	Reading	θ	x	$k_1 \times 10^2$	$k_4 \times 10^2$
1	42.5	0.0	0.000	—	—
2	41.55	6.7	0.006	—	—
3	39.2	22.8	0.019	0.16	5.42
4	36.6	42.8	0.034	0.15	5.35
5	34.1	63.3	0.048	0.15	5.24
6	29.2	100.0	0.077	0.16	5.81
7	26.7	137.0	0.091	0.15	5.27
8	23.2	183.0	0.112	0.14	5.23
Average					5.38

TABLE IV.
A, 0.246 ; B, 2.47 ; C, 1.56 ; D, 5.47 ; V, 0.6

No.	Reading	θ	x	$k_1 \times 10^2$	$k_4 \times 10^2$
1	42.0	0.0	0.000	—	—
2	38.2	2.5	0.022	—	—
3	35.4	5.0	0.039	1.32	2.87
4	31.3	8.9	0.063	1.25	2.49
5	26.3	15.1	0.092	1.29	3.21
6	21.6	22.0	0.119	1.27	3.16
7	17.8	29.7	0.142	1.22	3.19
8	13.9	40.0	0.165	1.18	3.09
9	9.55	56.5	0.190	1.30	3.09
10	4.95	88.5	0.217	1.03	2.96
11	1.70	139.0	0.236	0.99	2.98
Average					3.02

inversely proportional to the square of the concentration of the iodion.

Now as to the acid. In the experiments summarized in Table IV. the concentration of the acid is twice that in Table I. ; the value of k_1 has fallen from 2.15 to 1.25, or in the ratio of 1 to 0.58. In Table V. the concentration of the acid is $3/2$ that in Table IV., and the ratios of the constants are :

$$k_1(\text{Table IV.}) : k_1(\text{Table V.}) = 1.0 : 0.7.$$

From this it appears that when the quantity of acid present in the 600 cc is not less than 5 units, the rate is inversely pro-

portional to the concentration of the acid. This conclusion is supported by subsequent experiments (see Table XVII.), and the deviation observed in the case of Table I. must be attributed to the effect of the relatively large quantity of neutral salt on the dissociation of the acid.

TABLE V.

A, 0.246; B, 2.47; C, 1.56; D, 4.1; V, 0.6

No.	Reading	θ	A - x	$k_1 \times 10^3$	$k_4 \times 10^2$
1	41.1	0.0	0.246	—	—
2	40.2	2.0	0.241	—	—
3	36.1	7.33	0.216	8.76	2.08
4	30.95	15.0	0.185	8.77	2.11
5	23.65	29.0	0.141	8.52	2.18
6	20.35	37.3	0.122	8.43	1.86
7	17.45	46.7	0.104	8.10	2.14
8	14.15	58.7	0.0847	7.99	2.18
9	11.35	72.2	0.0680	7.82	2.06
10	7.25	116.0	0.0434	7.17	1.86
11	3.75	143.0	0.0224	7.29	2.16
12	2.30	179.0	0.0138	7.01	—
Average				2.07	

TABLE VI.

A, 0.492; B, 4.95; C, 3.11; D, 2.735; V, 0.6

No.	Reading	θ	A - x	$k_1 \times 10^2$	$k_4 \times 10^2$
1	41.1	0.0	0.492	—	—
2	40.4	3.16	0.484	—	—
3	38.05	6.83	0.456	0.71	3.15
4	34.25	13.66	0.410	0.68	3.24
5	30.35	21.66	0.363	0.67	3.25
6	26.33	31.83	0.315	0.65	3.29
7	22.63	43.5	0.271	0.62	3.11
8	19.4	57.5	0.232	0.59	2.99
9	14.7	84.3	0.176	0.54	2.85
10	9.5	118.3	0.114	0.56	3.01
11	8.03	134.2	0.0961	0.54	2.99
12	5.82	165.5	0.0697	0.47	3.73
Average				3.16	

Finally the experiments of Table I. were repeated, with the

same quantities of the four reacting substances, but dissolved in half the volume (in other words all four concentrations doubled). The value of k_1 (Table VI.) is in accordance with the conclusions of the preceding paragraphs.

Table VII. resembles Table VI., except that the concen-

TABLE VII.

A, 0.246 ; B, 4.95 ; C, 3.02 ; D, 5.47 ; V, 0.6

No.	Reading	θ	x	$k_1 \times 10^2$	$k_2 \times 10^2$
1	41.0	0.0	0.000	—	—
2	39.1	2.08	0.012	—	—
3	35.6	6.8	0.032	0.85	3.68
4	31.2	14.8	0.059	0.76	3.43
5	26.0	24.3	0.090	0.80	3.64
6	21.0	36.3	0.120	0.78	3.66
7	18.3	46.7	0.136	0.74	3.45
8	12.7	68.0	0.156	0.73	3.41
9	10.1	81.7	0.185	0.73	3.45
10	8.75	92.7	0.193	0.72	3.53
11	6.65	110.0	0.206	0.71	3.55
12	5.0	129.5	0.216	0.70	3.51
Average					3.51

tration of the triiodion is halved. In conformity with the conclusion reached by comparing k_1 and k_2 in Table I., this change has not affected the value of the constant.

Employing the notation of page 369, the results of the series of experiments just described may be condensed in the following expression, which connects the rate of the reaction with the concentrations of the reacting substances :

$$dx/d\theta = k_3 \frac{(A-x)/V \cdot (B-x)/V}{(C+x)^2/V^2 \cdot (D+x)/V} \quad \text{Eq. 7.}$$

Series B

For the purpose of ascertaining whether the effect of the various concentrations on the rate of the reaction was independent of wide variations in the quantities of the reagents present, a similar set of experiments (Tables VIII. to XII.) were carried out, in which the arsenious acid was present in much

TABLE VIII.

A, 2.46 ; B, 0.247 ; C, 2.99 ; D, 8.2 ; V, 0.6

No.	Reading	θ	x	$k_1 \times 10^3$	$k_4 \times 10^2$
1	41.2	0.0	0.000	—	—
2	38.7	11.0	0.015	—	—
3	36.0	25.0	0.031	2.04	2.13
4	31.6	46.5	0.057	2.32	2.17
5	27.5	71.5	0.082	2.30	2.23
6	24.0	96.6	0.103	2.25	2.22
7	19.6	136.0	0.129	2.15	2.17
Average				2.20	2.20

TABLE IX.

A, 4.92 ; B, 0.247 ; C, 2.99 ; D, 8.2 ; V, 0.6

No.	Reading	θ	x	$k_1 \times 10^3$	$k_4 \times 10^2$
1	20.6	0.0	0.000	—	—
2	19.8	2.16	0.009	—	—
3	17.0	13.7	0.043	5.9	2.7
4	15.9	26.5	0.061	4.4	1.9
5	12.6	46.3	0.091	4.4	1.8
6	10.4	69.3	0.122	4.2	1.9
7	8.7	89.5	0.143	4.1	1.9
8	7.3	104.0	0.159	4.2	1.9
9	6.1	118.0	0.174	4.4	2.0
10	5.0	136.0	0.187	4.5	2.1
11	3.0	176.0	0.211	4.7	2.2
Average				2.0	2.0

TABLE X.

A, 2.46 ; B, 0.247 ; C, 2.99 ; D, 3.865 ; V, 0.6

No.	Reading	θ	x	$k_1 \times 10^3$	$k_4 \times 10^2$
1	20.6	0.0	0.000	—	—
2	19.6	2.5	0.012	—	—
3	18.3	6.7	0.028	7.3	5.7
4	17.5	11.0	0.037	5.8	4.6
5	15.6	23.3	0.060	4.8	4.1
6	14.7	28.5	0.071	4.9	4.2
7	13.8	34.0	0.082	4.9	4.4
8	12.5	43.2	0.097	4.8	4.2
9	12.0	48.3	0.103	4.7	4.2
10	10.9	58.5	0.116	4.5	4.0
Average				4.2	4.2

TABLE XI.

A, 1.22; B, 0.124; C, 1.50; D, 4.10; V, 0.6

No.	Reading	θ	x	$k_1 \times 10^3$	$k_4 \times 10^2$
1	10.3	0.0	0.000	—	—
2	9.8	3.3	0.006	—	—
3	9.0	7.3	0.016	9.6	4.3
4	8.4	12.0	0.023	7.8	3.3
5	7.25	19.6	0.037	8.1	3.0
6	5.85	30.0	0.054	8.5	4.0
7	4.4	45.9	0.071	8.2	3.9
8	3.35	64.0	0.084	7.7	3.7
9	2.6	79.5	0.093	7.5	3.7
10	1.9	100.0	0.101	7.4	3.6
				Average	3.6

TABLE XII.

A, 2.46; B, 0.247; C, 2.01; D, 8.2; V, 0.6

No.	Reading	θ	B — x	$k_1 \times 10^3$	$k_4 \times 10^2$
1	20.6	0.0	0.247	—	—
2	19.7	2.66	0.236	—	—
3	18.8	7.0	0.225	4.5	1.93
4	16.2	16.7	0.194	6.1	2.46
5	14.9	25.3	0.179	5.3	2.09
6	13.1	39.5	0.157	4.8	1.99
7	11.9	50.0	0.143	4.6	1.93
8	9.3	72.0	0.112	4.7	1.96
9	7.2	95.0	0.086	4.8	2.08
10	5.1	129.0	0.061	4.7	2.07
11	2.6	194.0	0.031	4.6	2.18
				Average	2.09

smaller quantity than the other three. The results are presented in a condensed form in Table XVII. and, as will be seen, are in full accordance with the requirements of equation 7.

Series C

In order to have a series of measurements where the concentration of the acid was about the same as in the experiments on equilibrium of Table XXXIII., and in those on reduction of arsenic acid of Series D, I carried out a third series, whose results are contained of Tables XIII. and XIV.

TABLE XIII.

A, 0.256; B, 4.89; C, 1.69; D, 27.9; V, 0.6

No.	Reading	θ	A - x	$k_1 \times 10^3$	$k_4 \times 10^3$
1	43.1	0.0	0.256	—	—
2	33.7	2.5	0.200	—	—
3	32.8	7.5	0.195	2.35	3.12
4	28.5	20.25	0.169	3.55	5.39
5	24.1	35.0	0.143	4.46	5.76
6	21.6	48.5	0.126	4.37	5.89
7	18.4	63.0	0.109	4.35	5.93
8	15.5	79.7	0.092	4.37	5.80
9	13.7	94.5	0.0813	4.25	5.95
10	10.5	121.0	0.0647	4.15	5.92
11	4.4	271.0	0.0261	3.92	4.93
				Average	5.69

TABLE XIV.

A, 0.277; B, 4.89; C, 1.69; D, 62.3; V, 0.6

No.	Reading	θ	A - x	$k_1 \times 10^3$	$k_4 \times 10^3$
1	46.7	0.0	0.277	—	—
2	42.8	2.33	0.254	—	—
3	41.6	10.67	0.247	1.18	1.99
4	38.9	24.67	0.231	1.85	1.81
5	37.2	39.5	0.220	1.64	2.19
6	34.5	69.0	0.210	1.38	1.66
7	30.7	111.0	0.182	1.31	1.84
8	22.5	262.0	0.134	1.07	1.54
				Average	1.81

In the experiments of Table XIV. the concentration of the acid was $2\frac{1}{4}$ times as great as in those of Table XIII.; if the rate is inversely proportional to the concentration of the acid then

$$k_1(\text{Table XIV.}) = 4/9 \text{ of } k_1(\text{Table XIII.}) = 20 \times 10^{-4}.$$

If, on the other hand, the rate vary as the inverse square of the concentration, then

$$k_1(\text{Table XIV.}) = (4/9)^2 \text{ of } k_1(\text{Table XIII.}) = 9 \times 10^{-4}$$

The results of the trial were marred by slow deposition of

arsenious oxide during the measurements; to this is due the steady fall of k_t in Table XIV.; but its value at the beginning of the experiment (line 4, Table XIV., $k_t = 18.5 \times 10^{-4}$) leaves no doubt that the rate is inversely proportional to the first power, and not to the second power, of the concentration of the acid.

Other experiments

As it is not possible to prepare a solution in which the concentration of the triiodion is greatly in excess of that of the iodion, it was not possible to parallel Series A and B by a fourth in which the concentration of the iodion was small.

With regard to the acid, the experiments of Table I. made it seem very unlikely that simple results would be obtained from solutions in which the acid was present in small quantity; the more so, because in order to keep the rate within measureable limits, the concentration of the salts would have to be increased in proportion as that of the acid was lowered.

TABLE XV.

A, 0.500; B, 0.499; C, 0.500; D, 22.75; V, 0.6

No.	Reading		x	$k_4 \times 10^3$
1	41.6	0.0	0.0	—
2	41.0	1.83	0.007	4.92
3	39.25	4.83	0.029	7.04
4	37.1	9.5	0.054	6.95
5	34.9	15.16	0.081	7.37
6	31.65	26.7	0.120	7.49
7	29.0	39.0	0.152	7.64
8	25.45	62.5	0.194	7.58
9	23.55	79.5	0.217	7.61
10	20.55	113.0	0.253	7.79
11	19.1	140.0	0.271	7.64
Average				7.45

Finally, Table XV. gives the results of an experiment with equivalent quantities of arsenious acid, triiodion and iodion in presence of a large excess of acid. The constancy of k_4 may be regarded as further confirmation of the truth of equation 7.

Temperature coefficient

The experiments of Table XVI. were carried out at 10° C, all the others at 0° C. By comparing the values of k_3 from Tables XVI. and XVII., it will be seen that a rise in temperature of 10° C multiplies the rate by 3.5.

TABLE XVI.

A, 0.271; B, 0.979; C, 1.254; D, 22.75; V, 0.6

Temperature 10° C

No.	Reading	θ	A — x	$k_4 \times 10^2$
1	25.0	0.0	0.271	—
2	23.1	2.5	0.250	—
3	20.6	6.0	0.223	1.74
4	17.2	12.0	0.186	1.96
5	13.8	17.8	0.149	2.51
6	11.9	21.2	0.129	2.87
7	9.9	33.5	0.107	2.39
8	7.7	47.3	0.0835	2.41
9	5.85	59.3	0.0634	2.62
10	3.9	78.5	0.0423	2.84
11	3.0	95.3	0.0325	2.82
12	2.9	123.0	0.0314	2.20
Average				2.51

Résumé of Tables I–XVI.

In order to facilitate comparison, the initial compositions and the values of k_1 , k_3 , and k_4 from Tables I. to XVI. have been collected in Table XVII.

k_1 has been taken from line 4 of each table. k_4 is the average of all the values (except the first) in each table, and k_3 has been calculated from k_4 by the formula given on page 370.

The fact that k_3 does not vary in any regular manner with D is proof that the rate of the reaction remains proportional to the first power of the concentration of the acid up to the highest concentrations; while the constancy of k_3 from table to table is evidence of the accuracy of Equation 7.

TABLE XVII.

Table	A	B	C	D	V	$k_1 \times 10^2$	$k_4 \times 10^2$	k_3
I.	0.246	2.47	1.56	2.74	0.6	2.15	5.7	0.26
II.	0.246	4.95	1.56	2.74	0.6	4.25	6.4	0.29
III.	0.246	2.47	5.95	2.74	0.6	0.15	5.4	0.25
IV.	0.246	2.47	1.56	5.47	0.6	1.25	3.0	0.28
V.	0.246	2.47	1.56	8.20	0.6	0.88	2.1	0.29
VI.	0.490	4.95	3.11	5.47	0.6	0.68	3.2	0.29
VII.	0.246	4.95	3.02	5.47	0.6	0.76	3.5	0.32
VIII.	2.35	0.247	3.01	8.20	0.6	2.32	2.2	0.30
IX.	4.92	0.247	2.99	8.20	0.6	4.4	2.0	0.28
X.	2.46	0.247	2.99	3.87	0.6	5.8	4.2	0.27
XI.	1.22	0.124	1.50	4.10	0.6	7.8	3.6	0.25
XII.	2.46	0.247	2.01	8.20	0.6	6.1	2.1	0.29
XIII.	0.256	4.89	1.69	27.9	0.6	0.35	0.57	0.27
XIV.	0.277	4.89	1.69	62.3	0.6	—	—	—
XV.	0.500	0.499	0.500	22.75	0.6	—	0.75	0.28
XVI. ¹	0.271	0.979	1.254	22.75	0.6	—	2.51	0.95
Average (omitting XVI.)								0.28

PART II.

THE RATE OF REDUCTION OF ARSENIC ACID BY HYDROGEN IODIDE

The plan of these experiments is the same as that of Part I., my object being to determine the effect of changing the concentration of each reagent singly. Except in the experiments of Tables XVIII. and XIX. arsenic acid was chosen as the reagent to be present in small quantity, in order to avoid oxidation of the sodium thiosulphate during the titration.

The units and symbols defined on page 369 are employed in this part also, with the addition of the letter E to represent the number of units of arsenic acid initially present in any experiment. The sign of x has been changed, so that in Part II. x represents the number of units of arsenious acid formed by the reduction of arsenic acid.

To the constants there has been added k_5 , defined as follows :

$$dx/d\theta = k_5 V^{-3} (C - x)(D - x)(E - x).$$

¹ Temperature 10° C. All the others, 0° C.

METHOD OF CARRYING OUT THE EXPERIMENTS

The reaction was carried out in flasks kept at 0°C by a bath of snow and water. The solution for the reaction was prepared in two parts which were cooled to 0°C before mixing. In one flask half the sulphuric acid was added to the potassium iodide and part of the water; in the other flask the arsenic acid was mixed with the remainder of the sulphuric acid and water. By thus dividing the acid I avoided a rise in temperature when the contents of the flasks were mixed and the reaction commenced. Any iodine liberated in the first flask (owing to the action of the air on the acid solution of potassium iodide) was determined and allowed for. Owing to the short duration of most of the experiments no more elaborate precautions against the action of air seemed necessary; but to make sure, the experiments in Table XXIV*a*. were carried out with solutions freed from air and kept under carbon dioxide. The constants calculated from these experiments are almost identical with those of Table XXIV., where no such precautions were taken.

The experiments of Tables XXVIII. and XXIX., where the rate of reaction was measured over an interval of 50 hours, were carried out in test-tubes filled with carbon dioxide and sealed.

The progress of the reaction was determined at intervals by measuring out 10 cc of the reacting mixture, diluting it to 10 or 20 times its volume, in order to stop the reaction and reduce the concentration of the acid; and then quickly titrating with sodium thiosulphate. For the reasons given on page 371 excess of sodium thiosulphate was avoided.

RESULTS OF THE MEASUREMENTS**Series D**

The constancy of k_1 in each of the tables (in Table XXI. k_2 is calculated for comparison) shows that the rate is proportional to the first power of the concentration of the arsenic acid. Evidence that this law holds for higher concentrations as well, is afforded by the experiments of Tables XVIII. and XIX,

(where the reagent present in small quantity is iodion); in one of these the quantity of arsenic acid present is twice that in the other, and the values of k_1 stand in the same proportion.

TABLE XVIII.

C, 0.1385; D, 22.85; E, 1.16; V, 0.12

No.	Reading	θ	x	$C - x$	$k_1 \times 10^3$	$k_5 \times 10^6$
1	0.0	0.0	0.0	0.1385	—	—
2	4.0	1.2	0.0095	0.129	—	—
3	7.25	3.7	0.0172	0.121	9.2	1.70
4	10.7	6.2	0.0255	0.113	15.9	1.47
5	15.2	10.5	0.0361	0.102	10.8	1.65
6	21.7	17.5	0.0515	0.087	10.5	1.65
7	25.0	28.2	0.0594	0.079	7.8	1.21
8	27.3	38.0	0.0648	0.0737	6.6	1.30

58.3 cc sodium thiosulphate solution is equivalent to 0.1385 units I_3 .

TABLE XIX

C, 0.1385; D, 22.85; E, 0.580; V, 0.12

No.	Reading	θ	x	$C - x$	$k_1 \times 10^3$	$k_5 \times 10^6$
1	0.0	0.0	0.0	0.1385	—	—
2	2.8	1.0	0.00665	0.132	—	—
3	5.3	4.2	0.0125	0.126	6.24	1.84
4	9.5	10.7	0.0226	0.116	5.75	1.68
5	15.2	20.0	0.0361	0.102	5.79	1.83
6	18.0	27.0	0.0427	0.096	5.35	1.65
7	22.0	37.7	0.0523	0.0862	5.02	1.61
8	24.2	46.7	0.0575	0.0810	4.64	1.48
9	25.8	58.7	0.0613	0.0772	4.02	1.30

58.3 cc sodium thiosulphate solution is equivalent to 0.1385 units I_3 .

TABLE XX.

C, 5.64; D, 9.4; E, 0.290; V, 0.13

No.	Reading	θ	x	$E - x$	$k_1 \times 10^3$
1	0.0	0.0	0.0	0.290	—
2	3.45	2.7	0.0224	0.268	—
3	11.65	10.8	0.0602	0.230	8.2
4	16.3	17.0	0.106	0.184	11.4
5	19.8	22.5	0.1288	0.161	11.2
6	23.6	29.0	0.153	0.137	11.1
7	27.3	37.2	0.177	0.113	10.9
8	29.9	43.8	0.194	0.096	10.9
9	31.9	50.5	0.207	0.083	10.7
10	34.3	59.3	0.223	0.067	10.6
11	37.2	73.0	0.242	0.048	10.6
12	39.2	87.5	0.255	0.035	10.4
13	41.4	108.0	0.269	0.021	10.5

44.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_3 .

TABLE XXI.

C, 3.76; D, 9.4; E, 0.290; V, 0.13

No.	Reading	θ	x	$E - x$	$k_1 \times 10^3$	$k_2 \times 10^2$
1	0.0	0.0	0.0	0.290	—	—
2	1.7	2.2	0.0109	0.279	—	—
3	7.55	12.8	0.0486	0.241	6.0	5.33
4	9.3	16.5	0.0598	0.230	5.87	5.34
5	13.9	27.0	0.0894	0.201	5.72	5.56
6	17.95	37.3	0.115	0.175	5.78	6.07
7	22.75	52.5	0.146	0.144	5.71	6.68
8	28.5	76.5	0.184	0.106	5.65	7.87
9	33.2	103.0	0.213	0.077	5.54	9.31
10	37.0	134.0	0.238	0.052	5.53	11.9
11	39.8	167.0	0.256	0.034	5.54	15.6
12	42.5	218.0	0.273	0.017	5.65	25.5

45.1 cc sodium thiosulphate solution is equivalent to 0.290 units I_3 .

TABLE XXII.

C, 1.288; D, 22.85; E, 0.136; V, 0.12

No.	Reading	θ	x	$E - x$	$k_1 \times 10^3$
1	0.0	0.0	0.0	0.136	—
2	1.8	1.33	0.0066	0.129	—
3	3.8	5.3	0.0140	0.122	6.3
4	12.5	10.3	0.0460	0.090	17.4
5	18.1	17.0	0.0666	0.069	17.2
6	25.1	28.5	0.0923	0.044	17.3
7	30.3	42.2	0.1114	0.025	17.5
8	32.8	53.2	0.1206	0.015	17.7

37.0 cc sodium thiosulphate solution is equivalent to 0.136 units I_3 .

TABLE XXIII.

C, 0.644; D, 22.85; E, 0.136; V, 0.12

No.	Reading	θ	x	$E - x$	$k_1 \times 10^3$
1	0.0	0.0	0.0	0.136	—
2	1.05	1.66	0.00386	0.132	—
3	8.85	15.5	0.0326	0.103	7.68
4	12.5	25.5	0.0460	0.090	7.77
5	16.7	35.7	0.0614	0.075	7.32
6	20.4	48.3	0.0751	0.061	7.21
7	23.7	64.0	0.0871	0.049	6.94
8	26.9	87.0	0.0989	0.037	6.47
9	29.8	116.0	0.1095	0.026	6.13
10	31.9	161.0	0.1173	0.019	5.83
11	32.8	198.0	0.1206	0.015	3.84

37.0 cc sodium thiosulphate solution is equivalent to 0.136 units I_3 .

In Tables XX., XXI., XXII., and XXIII. are given the results obtained by varying the concentration of the iodion. In the first pair, where the concentrations are highest, adding fifty percent to the iodion doubles the rate; in the second pair, doubling the iodion multiplies the rate by about two and a quarter. Thus the "order of the reaction with respect to iodion" decreases with decrease in the concentration of that reagent. Even in Tables XVIII. and XIX. the rate seems to fall

TABLE XXIV.

C, 1.88; D, 18.25; E, 0.290; V, 0.13

No.	Reading	θ	x	$E - x$	$k_1 \times 10^3$
1	0.0	0.0	0.0	0.290	—
2	2.85	2.5	0.0185	0.271	—
3	8.1	8.3	0.0527	0.237	10.0
4	12.9	14.5	0.0838	0.206	9.92
5	17.8	22.2	0.116	0.174	9.77
6	21.8	29.3	0.142	0.148	9.81
7	25.2	37.0	0.164	0.126	9.65
8	29.9	47.3	0.194	0.096	10.0
9	32.2	59.0	0.209	0.081	9.27
10	36.3	76.3	0.236	0.064	8.50
11	40.7	111.0	0.265	0.025	9.63

44.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_3 .

TABLE XXIVa.

C, 1.88; D, 18.25; E, 0.290; V, 0.13

All solutions were free of air and the experiment was carried out under an atmosphere of carbon dioxide.

No.	Reading	θ	$k_1 \times 10^3$
1	0.0	0.0	—
2	3.35	2.3	—
3	7.05	6.7	9.4
4	12.0	12.5	10.0
5	15.5	17.3	10.1
6	19.0	22.7	10.1
7	22.1	28.5	10.0
8	25.3	35.0	10.1
9	28.9	44.3	10.0
10	32.0	54.3	9.9
11	34.9	67.0	9.7

44.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_3 .

TABLE XXV.

C, 1.88; D, 13.7; E, 0.290; V, 0.13

No.	Reading	θ	x	$E-x$	$k_1 \times 10^3$
1	0.0	0.0	0.0	0.290	—
2	1.5	1.5	0.00975	0.280	—
3	4.7	8.0	0.0307	0.259	5.22
4	7.7	14.8	0.0501	0.240	5.03
5	10.4	21.7	0.0677	0.222	4.99
6	12.5	27.3	0.0813	0.209	4.92
7	16.5	39.7	0.1073	0.183	4.84
8	20.8	55.0	0.135	0.155	4.80
9	24.2	70.3	0.157	0.133	4.70
10	28.0	89.8	0.182	0.108	4.69
11	32.1	119.0	0.208	0.082	4.50
12	36.2	160.0	0.235	0.055	4.47

44.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_3 .

TABLE XXVI.

C, 1.88; D, 9.15; E, 0.290; V, 0.13

No.	Reading	θ	x	$E-x$	$k_1 \times 10^3$
1	0.0	0.0	0.0	0.290	—
2	1.3	3.0	0.0085	0.281	—
3	2.15	7.5	0.0140	0.276	1.73
4	4.75	20.3	0.0309	0.259	2.04
5	7.95	37.5	0.0517	0.238	2.09
6	10.6	52.7	0.0689	0.221	2.09
7	14.9	83.0	0.0967	0.193	2.04
8	18.9	112.0	0.123	0.167	2.07
9	21.7	137.0	0.141	0.149	2.05
10	25.6	179.0	0.166	0.124	2.02
11	29.3	223.0	0.191	0.099	2.06
12	32.7	279.0	0.212	0.078	2.02

44.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_3 .

TABLE XXVII.

C, 3.76; D, 4.70; E, 0.290; V, 0.13

No.	Reading	θ	x	$E - x$	$k_1 \times 10^3$
1	0.0	0.0	0.0	0.290	—
2	0.85	2.0	0.00553	0.284	—
3	3.9	19.0	0.0252	0.265	1.85
4	7.4	41.5	0.0482	0.242	1.78
5	11.05	68.0	0.0719	0.218	1.76
6	15.5	104.5	0.1007	0.189	1.72
7	19.1	139.0	0.124	0.166	1.71
8	22.4	175.0	0.146	0.144	1.71
9	29.2	262.0	0.190	0.100	1.74
10	31.2	302.0	0.203	0.087	1.71
11	33.3	351.0	0.217	0.073	1.69
12	35.8	414.0	0.233	0.057	1.69
13	38.3	490.0	0.249	0.041	1.70

44.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_3 .

TABLE XXVIII.

C, 2.270; D, 2.293; E, 0.310; V, 0.155

No.	Reading	θ	x	$E - x$	$k_3 + 10^7$	$k_1 \times 10^4$
1	0.0	0.0	0.0	0.310	—	—
2	0.35	10.0	0.00161	0.308	—	—
3	2.3	66.0	0.0107	0.299	3.84	2.30
4	2.65	74.0	0.0122	0.298	4.22	2.51
5	9.45	296.0	0.0434	0.267	3.62	2.17
6	24.6	994.0	0.113	0.197	3.22	1.97
7	26.6	1177.0	0.122	0.188	3.17	1.83
8	29.7	1432.0	0.137	0.173	3.07	1.77
9	35.8	2480.0	0.164	0.137	2.61	1.43
10	37.3	2880.0	0.171	0.130	2.34	1.31

Average 3.26

67.5 cc sodium thiosulphate solution is equivalent to 0.310 units I_3 .

TABLE XXIX.

C, 2.270; D, 1.147; E, 0.310; V, 0.155

No.	Reading	θ	x	$E - x$	$k_5 \times 10^7$	$k_1 \times 10^4$
1	0.0	0.0	0.0	0.310	—	—
2	0.2	9.5	0.00092	0.309	—	—
3	1.2	70.0	0.00551	0.304	3.54	1.17
4	3.7	292.0	0.0170	0.293	2.72	0.819
5	13.1	991.0	0.0602	0.250	3.19	0.938
6	14.8	1175.0	0.0680	0.242	3.04	0.906
7	16.9	1430.0	0.0776	0.232	3.05	0.873
8	21.6	2470.0	0.0989	0.211	2.38	0.675
9	22.4	2880.0	0.102	0.208	2.13	0.599

Average 2.88

67.5 cc sodium thiosulphate solution is equivalent to 0.310 units I_3 .

TABLE XXX.

C, 1.88; D, 18.75; E, 0.290; V, 0.26

No.	Reading	θ	x	$E - x$	$k_1 \times 10^4$
1	0.0	0.0	0.000	0.290	—
2	0.9	2.5	0.006	0.284	—
3	2.35	18.7	0.0153	0.275	8.64
4	4.15	38.0	0.0269	0.263	9.38
5	6.55	66.8	0.0426	0.247	9.42
6	9.4	99.8	0.0611	0.229	9.61
7	11.6	131.0	0.0745	0.215	9.45
8	14.4	176.0	0.0936	0.196	9.31
9	15.9	197.0	0.1034	0.187	9.33

44.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_3 .

off more rapidly than the concentration of the iodion — at least, the “constant” k_5 , calculated on the assumption that the rate is proportional to the concentrations of the iodion and of the arsenic acid, certainly diminishes as the reaction progresses.

In the case of the acid the effect of concentration on the order is even more marked. Comparing Tables XXIV., XXV., and XXVI.; XXI. and XXVII.; and XXVIII. and XXIX., it

is apparent that the order falls from well over the second, to almost the first, while the concentration of the acid decreases in the ratio 16:1. That this is not due to changes in the dissociation of the sulphuric acid, is evidenced by the fact that nothing analogous was found in the reaction between arsenious acid and triiodine; it may, however, be ascribed to a change in the dissociation of the arsenious acid as the concentration of the sulphuric acid is increased. The reactions would then take place according to the equation



This explanation does not necessarily assume that the ions of arsenious and arsenic acids which I have selected for use in the chemical equations are those "actually present and reacting," but only that when the concentration of the hydrogen ions is below a certain limit the ions of the arsenious and arsenic acids contain an equal number of hydrogen atoms, while above that limit hydrogen is taken up more rapidly by the arsenious ion than by the arsenic ion. This is in full accord with what we know of the relative strengths of the two acids; the polymeric formulas of the acids however receive no support from these results.

TABLE XXXI.

C, 0.941; D, 11.7; E, 1.16; V, 0.12

Temperature 10° C

No.	Reading	θ	x	$k_5 \times 10^7$
1	0.0	0.0	0.0	—
2	2.9	1.7	0.0316	—
3	6.2	4.2	0.0676	4.9
4	8.5	6.5	0.0926	8.8
5	13.3	11.5	0.145	5.9
6	17.7	16.7	0.193	8.0
7	20.5	22.0	0.224	6.8
8	22.3	27.5	0.243	6.0
9	25.9	33.5	0.282	6.2
10	30.6	40.3	0.334	6.6
11	34.8	48.5	0.377	6.5
12	36.5	56.0	0.398	6.3
Average				6.8

1 cc sodium thiosulphate solution is equivalent to 0.0109 units I_3 .

TABLE XXXII.

C, 0.842; D, 11.8; E, 1.16; V, 0.12

No.	Reading	θ	x	$k_5 \times 10^7$
1	0.0	0.0	0.0	—
2	2.85	8.5	0.0408	—
3	4.6	15.8	0.0658	1.5
4	6.3	23.0	0.0905	3.6
5	8.9	35.0	0.127	3.2
6	10.8	48.3	0.155	2.9
7	12.7	63.8	0.182	3.0
8	14.7	81.8	0.210	2.8
9	18.8	111.0	0.269	2.9
Average				3.1

1 cc sodium thiosulphate solution is equivalent to 0.0143 units I_2 .

Temperature coefficient

Comparing Tables XXXI. and XXXII., it appears that a rise of 10° C multiplies the rate by 2.2.

PART III.

EQUILIBRIUM

A priori considerations, and the results of some preliminary experiments made it seem probable that at equilibrium the relation¹

$$K_6 V^4 = \frac{(E + x)(D + x)^2(C + x)^3}{(A - x)(B - x)} \quad \text{Eq. 8.}$$

would subsist between the concentrations of the reagents.

The change in the concentration of triiodion needed to balance given changes in the concentrations of each of the other con-

¹ A, B, C, D, E, x , V have the meanings assigned on page 382. The signs + and — must be interchanged if the reaction leading to equilibrium involves the formation instead of the disappearance of triiodion.

stituents was determined quite sharply by keeping the quantity of that reagent in the mixture small, in comparison with those of the others; the concentrations of the latter being thus almost unaffected by reactions taking place in the solution.

The interpretation of the results was still further simplified by making up the mixtures according to a plan described under "Series E."

METHOD OF CARRYING OUT THE EXPERIMENTS

As a criterion that the solutions had actually reached a state of equilibrium, it was obviously not sufficient to make sure that their compositions remained unaltered for a longer or shorter period of time; such evidence would not exclude cases of "false equilibrium." It was necessary therefore to make up solutions containing the same total weights of arsenic, potassium iodide, iodine, sulphuric acid, and water; in one of which the components were originally present as arsenious acid, triiodion, iodion and acid, and in the other as arsenic acid, iodion and acid.

To avoid loss of iodine by evaporation, the experiments were carried out in stoppered bottles. In each case two bottles were prepared, using the same volumes of the various stock solutions (page 370), but in one of them the order of mixing was: Sodium arsenite, sulphuric acid, iodide, iodine, and water to make up the volume; and in the other: Sodium arsenite, iodine, iodide, sulphuric acid, and water to make up the same volume.

So that in the first case the arsenious acid was slowly oxidized by the triiodion, and in the second the arsenic acid formed by the instantaneous reaction between sodium arsenite and triiodion was slowly reduced by the hydriodic acid.

Final analyses were carried out only when the quantity of triiodion was the same in the two mixtures within one percent; a period of less than twenty-four hours was quite sufficient for the purpose.

Direct titration of the triiodion in the solution by sodium thiosulphate was not feasible; as in the absence of triiodion the reaction between arsenic acid and hydriodic acid was rapid

enough to affect the result. It was found, however, that by pouring into the solution to be analyzed a solution of thiosulphate in quantity sufficient to remove almost all the triiodion, mixed with water to slow the rate of reduction of the arsenic acid, the titration could be brought to a satisfactory conclusion. For the reasons given on page 371, excess of thiosulphate was avoided. If after the conclusion of the analysis at least one minute elapsed before reappearance of the blue color of iodide of starch, it was evident that the water had been added in sufficient quantity.

Two analyses were made of the solution in each bottle; and consequently four determinations of each equilibrium point.

RESULTS OF THE MEASUREMENTS

Series E

Having found by trial the proportions in which the stock solutions might be mixed so that only a very slight reaction was necessary to bring the system to equilibrium ("standard" mixture), I prepared a set of bottles¹ in which the concentration of the triiodion was twice that of the standard, while the concentration of the iodion was $\frac{1}{2}$, $\frac{2}{3}$, and $\frac{4}{5}$ times the standard respectively. In the first, the amount of triiodion increased, and in the third decreased, while in the second it remained stationary. From this it is obvious without further calculation that the third power of the concentration of the iodion must appear in the equilibrium constant.

The same method was employed with the other reagents and with the volume; finally the value of K_6 (Eq. 8) was calculated from each experiment.

A glance at Table XXXIII. shows that the requirements of Equation 8 are satisfied. The greatest deviation is in the case of the iodion, for which the third power of the concentration seems, if anything, a trifle high. This is in line with the observation made in discussing Series A (page 373), that multiplying the

¹ Nos. 4, 5, and 6 of Table XXXIII. No. 1 is standard.

concentration of the iodion by four divided k_1 by fourteen instead of by sixteen.

TABLE XXXIII.¹

No.	A - x	B - x	C + x	D + x	E + x	V	$K_8 \times 10^{-4}$
1	0.01857	0.3424	0.5689	1.140	0.4016	0.1	15.1
2	0.03607	0.3432	0.5750	1.612	0.4008	0.1	16.1
3	0.03098	0.3381	0.5801	1.446	0.4059	0.1	15.8
4	0.04792	0.3260	0.7958	1.127	0.3890	0.1	14.2
5	0.0381	0.3452	0.7198	1.137	0.3988	0.1	14.6
6	0.03346	0.3411	0.6856	1.141	0.4029	0.1	14.8
7	0.03941	0.3465	0.5717	1.136	0.801	0.1	14.1
8	0.03509	0.1720	0.5760	1.138	0.4018	0.1	16.5
9	0.01635	0.1699	0.5712	1.139	0.4039	0.1189	17.7
10	0.0198	0.1734	0.5677	1.136	0.4004	0.1149	16.1
11	0.0212	0.1748	0.5663	1.135	0.3990	0.1123	15.8
12	0.01903	0.3428	0.5685	1.139	0.4012	0.1	14.6
13 ²	0.01113	0.3349	0.5652	1.147	0.4091	0.1	26.1
14	0.01787	0.3412	0.5596	1.130	0.4023	0.1	14.8
15	0.01646	0.1701	0.5678	1.135	0.4037	0.1189	17.0
16	0.01354	0.1698	0.5644	1.132	0.4003	0.1260	15.9

TABLE XXXIV.

No.	A	A - x	B - x	C + x	D + x	E + x	V
1	0.0384	0.0384	0.4836	0.1991	10.80	0.0985	0.1
2	0.0768	0.0909	0.5036	0.1801	14.49	0.0785	0.1
3	0.0768	0.0844	0.4971	0.1866	13.72	0.0850	0.1

Series F

On finding that the effect which doubling the concentration of the sulphuric acid produced on the rate of reduction of arsenic

¹ No. 1 is the standard. In Nos. 9 to 16, A was the same as in No. 1; in Nos. 2 to 8, A was twice as great as in No. 1.

² Temperature 20° C. All other experiments of Part III, temp. 0°C.

acid was dependent on the concentration of the sulphuric acid (Series D), I undertook the experiments of Table XXXIV. in order to determine whether the conditions of equilibrium were affected by the same circumstance. The measurements show clearly that when the acid is present in large quantity, the third or a higher power of its concentration and not the second power must be introduced into the equation of equilibrium.

Temperature coefficient

Experiments Nos. 12 and 13 of Table XXXIII. were carried out with different portions of the same solutions, No. 13 at 20° C, and No. 12 (like all the others of the table) at 0° C. A rise of 20° C thus almost doubles the constant. From the experiments of Parts I. and II. a rise of 10° multiplies the quotient k_3/k_5 by 1.6, which is not far from 1.4, the square root of 2.

Relation between k_3 , k_5 , and K_6

According to the theory explained in the Introduction, the constants of the two rates and that of equilibrium should be connected by the relation

$$K_6 = \frac{k_3}{k_5}.$$

Introducing the values $k_3 = 0.28$ (Table XVII.), and $k_5 = 3.26 \times 10^{-7}$ (Table XXVIII.) gives 8.6×10^5 as the "calculated" value of K_6 ; while direct experiment (Table XXXIII.) gives $K_6 = 1.5 \times 10^5$. The two numbers are thus of the same order of magnitude.

In selecting k_5 I was forced to use the data of Table XXXIII., as it is only when the concentration of the acid is low that the rate obeys the law of paragraph iii of the introduction. The large amount of salt present in this experiment (three molecules of potassium iodide to one of sulphuric acid) was introduced in order to make the rate quick enough to measure. Perhaps the considerable numerical discrepancy between k_3/k_5 and K_6 is due in part to this circumstance.

CONCLUSION

The results of my experiments can only be regarded as a very striking confirmation of the Theory of Kinetic Equilibrium.

In Part I. it is shown that the reaction between arsenious acid and iodine in acid solution proceeds according to the scheme¹

$$dx/d\theta = k.a.b/.x.y.^2z$$

The "order" of the rate of the reverse reaction, however (Part II.), depends on the concentrations of the reagents; in comparatively dilute solutions it is of the third order,

$$-dx/d\theta = k'.x.y.z,$$

but if the concentration of the iodide or of the acid be increased, higher powers of y and z must be introduced into the equation.

Finally, in Part III. it is shown that the condition of equilibrium of Eq. 4

$$K = \frac{a.b}{x.y^3.z^2}$$

holds only for the dilute solutions, where the reverse reaction is of the third order,² and that in the case of solutions containing a greater proportion of acid a higher power of z must be introduced.

Thus for dilute solutions my experiments on the rates of the two reactions and on the equilibrium between them are in full accord with the theory developed in paragraph iii of the Introduction. For solutions containing larger quantities of acid, the expression for the rate of oxidation of arsenious acid remains the same, while the change in the form of the equilibrium function is parallel to that in the expression for the rate of reduction of arsenic acid; on page 391 I have suggested a plausible explanation of the changes in question.

The quotient of the two rate constants is of the same order of magnitude as the equilibrium constant (page 396); and the few experiments carried out at higher temperatures show that the temperature coefficient of the equilibrium constant accords, both

¹ Using the symbols of page 367.

² In the experiments of Table XX. it is of the fifth order.

in sign and in magnitude, with the quotient of the temperature coefficients of the two rates (page 396). Owing to the conditions under which the measurements were carried out, a closer agreement could hardly be expected.

In conclusion, I wish to express my thanks to Prof. W. Lash Miller, at whose suggestion this research was undertaken, and under whose direction it has been carried out.

*University of Toronto,
July, 1902.*

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