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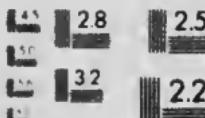
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THE RATE OF THE REACTION BETWEEN ARSENI-
OUS ACID AND IODINE IN ACID SOLUTION;
THE RATE OF THE REVERSE REAC-
TION; AND THE EQUILIBRIUM
BETWEEN THEM.

THESIS

PRESENTED TO THE SENATE OF THE UNIVERSITY OF
TORONTO, FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY,

BY

JOHN R. ROEBUCK.

THE RATE OF THE REACTION BETWEEN ARSENIOUS ACID AND IODINE IN ACID SOLUTION; THE RATE OF THE REVERSE REACTION; AND THE EQUILIBRIUM BETWEEN THEM.

Thesis

BY

JOHN R. ROEBUCK

To the Senate of the University of Toronto:

I beg to report that Mr. John R. Roebuck, a candidate for the Degree of Doctor of Philosophy, has passed a satisfactory examination in Physical Chemistry, his major subject; and I recommend that his thesis, " The Rate of the Reaction between Arsenious Acid and Iodine in acid solution; the Rate of the Reverse Reaction; and the Equilibrium between them" be accepted for the degree.

W. LASH MILLER,
Toronto, May, 1906.   Associate-Professor of Physical Chemistry.

I hereby certify that the thesis above mentioned has been accepted by the Senate of the University of Toronto for the Degree of Doctor of Philosophy, in accordance with the terms of the statute in that behalf.

The University of Toronto,   JAMES BREBNER,
June 5, 1906.   Registrar.

THE RATE OF THE REACTION BETWEEN ARSENIOUS ACID AND IODINE IN ACID SOLUTION; THE RATE OF THE REVERSE REACTION; AND THE EQUILIBRIUM BETWEEN THEM.

— — —

BY J. R. ROEBUCK.

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."*

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

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

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

corresponding to the chemical equation for the reaction

$$aA + bB + cC + \ldots = dD + eE + \ldots$$

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

Under these circumstances, it is worth while to examine the funda-
ments of the theory somewhat critically. The introduction of the in-
dices into Eq. 2 is based on the so-called "kinetic view of chemical
equilibrium," viz.: that in a system at equilibrium the two opposite re-
actions are still taking place, but at equal rates. According to this
view the concentration function of Gu'dberg and Waage's equation is
to be regarded as the quotient of two other concentration functions be-
longing 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 reac-
tion, 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 com-
pounds."

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 measure-
ment.

The "ordinary" chemical equation representing this reaction is

$$H_3AsO_3 + I_2 + H_2O = H_3AsO_4 + 2HI.$$
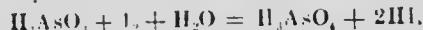
Adopting the notation of the ion theory, this equation may be written [2]

$$AsO_3 + I_3 + H_2O = AsO_4 + 3I + 2H, \qquad \text{Eq. 3.}$$
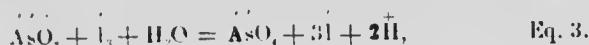
and the condition of equilibrium is:

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

(where a represents the concentration of the AsO_4, b that of the I, 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.

[1] phys. Chem. 22, 268 (1897).
[2] Nothing certain is known as to the ions in a solution of arsenious acid.
See page 391.

Predictions of the theory

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

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

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 action (reduction of arsenic acid by hydrogen iodide) should be in accordance with Eq. 6; and the "explanation" would be furnished 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 $I_3 = I_2 + I$, this may be explained by the chemical reaction:

$$As O_3 + I_2 + H_2O = AsO_4 + 2I + 2H.$$
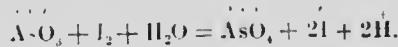
(iii) $a.b/y^2.z$ and $1/x.y.z$; assuming the instantaneous reactions $I_3 = I_2 + I$, and $I_2 + OH = IOH + 2I$, this may be explained by the chemical equation:

$$AsO_3 + HOI = AsO_4 + H + I.$$

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

$$AsO_3 + OI = AsO_4 + I.$$

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

---

[1] Some of the possible factorings obviously cannot correspond to kinetic equations. To choose an extreme case, a, and $b/x.y^2.z^4$.

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

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

and

$$2I_3 + H_2O = 1O_2H + 5I + 3\overset{+}{H} \text{ (instantaneous)}$$

$$2AsO_3 + 1O_2H = 2AsO_4 + I + \overset{+}{H}.$$
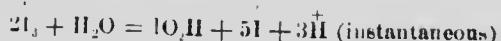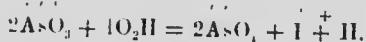
(VI) Finally both numerator and denominator of the fraction of Eq. 4 may be multiplied by one and the same quantity (for instance by z), and the product may be factored. Under this head would come explanations based on "catalysis by hydrogen ions," etc., etc.

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 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 1.

THE RATE OF OXIDATION OF ARSENIOUS 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.)

---

[1] In the tables of Series B, A in this formula was replaced by B

in calculating the 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 × 49.4 1000 units AsO_3, and soda sufficient to neutralize 50 × 0.0396 1.98 units of sulphuric acid; iodine solution 5 cc, containing 5 × 49.2 1000 0.246 units triiodion, and 5 × 17.6 1000 0.088 units iodion; potassium iodide solution 50 cc, containing 50 × 29.3 1000 1.47 units iodion; sulphuric acid, 10 cc 9.13 n.acid 1.715 units; water, 185 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, 1.715 — 1.98   2.335 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 litre. I accordingly restricted[1] 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 completed without excess of thiosulphate. I en-

[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.

deavored 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_1 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 arsenious

TABLE I.

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

No.	Reading	θ	A r	$k_1 \times 10^2$	$k_4 \times 10^2$	$k_2 \times 10$
1	42.6	0.0	0.216			—
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	0.0661	1.97	5.57	4.56
9	9.4	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	15 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. 1.95; C. 1.56; D. 2.735; V. 0 6

No.	Reading	θ	A r	$k_1 \times 1 .$	$k_4 \times 10^2$
1	42 7	0.0	0.246		
2	23.2	3.8	0 131		
3	18 65	6.3	0.1074	3.40	5.33
4	11.35	8.67	0.0827	1 25	6 08
5	10.4	11 7	0.0599	4.40	6.40
6	8.15	11.2	0 0470	4 37	6.48
7	6.55	16.3	0.0377	4 39	6.59
8	4 4	20.8	0.0254	1.25	6. 15
9	3.5	23.0	0.0202	3.86	6.55
10	1.85	30.0	0 0107	4.20	—
				Average	6.4

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 inversely propor   l to the square of the concentration of the iodion.

TABLE III.

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

No.	Reading	θ	x	$k_1 \times 10$	$k_4 \times 10^2$
1	42.5	0.0	0.000		
2	41.55	6.7	0.006		
3	39.2	22.8	0.019		
4	36.6	42.8	0.03?	0.16	5.42
5	34.1	63.3	0.048	0.15	5.35
6	29.2	1?0.0	0.077	0.15	5.24
7	26.7	137 9	0.091	0.16	5.81
8	2?.2	183.0	0.112	0.15	5.27
				0.14	5.?3
				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	3.2?
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

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 ? that in Table IV., and the ratios of the constants are:

$$k_1(\text{Table IV.}) : k_1(\text{Table V.}) = 1.0 : 0.?.$$

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 proportional 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	$A-x$	$k_1 \times 10^2$	$k_4 \times 10^2$
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	19.1	57.5	0.232	0.59	2.99
9	14.7	81.3	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

J. R. Roebuck

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 concentration of

TABLE VII.

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

No.	Reading	h	x	$k_1 \times 10^2$	$k_1 \times 10^2$
1	41.0	0.0	0.000		
2	39.1	2.08	0.012		
3	35.6	6.8	0.032		
4	31.2	14.8	0.059	0.85	3.68
5	26.0	24.3	0.090	0.76	3.43
6	21.0	36.3	0.120	0.80	3.64
7	18.3	46.7	0.136	0.78	3.66
8	12.7	68.0	0.156	0.71	3.45
9	10.1	81.7	0.185	0.73	3.44
10	8.75	92.7	0.193	0.53	3.45
11	6.65	110.0	0.206	0.72	3.53
12	5.0	129.5	0.216	0.71	3.55
				0.70	3.54
				Average	3.54

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:

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

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 smaller quantity than the other three. The

Table VIII.
A, 2.16; B, 0.217; C, 2.99; D, 8.2; V, 0.6

No.	Reading	θ	x	$k_1 \times 10^4$	$k_4 \times 10^2$
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

Table IX.
A, 1.92; B, 0.217; C, 2.99; D, 8.2; V, 0.6

No.	Reading	θ	r	$k_1 \times 10^4$	$k_4 \times 10^2$
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	10.1	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	1.4	2.0
10	5.0	136.0	0.187	4.5	2.1
11	3.0	176.0	0.211	1.7	2.2
				Average	2.0

Table X.
A, 2.16; B, 0.247; C, 2.99; D, 3.865; V, 0.6

No.	Reading	θ	x	$k_1 \times 10^2$	$k_4 \times 10^2$
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	1.8	1.1
6	14.7	28.5	0.071	1.9	4.2
7	13.8	34.0	0.082	4.9	4.1
8	12.5	43.2	0.097	1.8	4.2
9	12.0	48.3	0.103	1.7	1.2
10	10.9	58.5	0.116	4.5	4.0
				Average	4.2

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Table XI.

A. 1 22: B 0.121: C. 1 50: D. 4.10: V. 0.6

No.	Reading	θ	x	$k_1 \times 10^2$	$k_4 \times 10^2$
1	10.3	0.0	0.000		
2	9 8	3 3	0.006		
3	9.0	7.3	0.016		
4	8 4	12 0	0.023	9.6	4 3
5	7 25	19.6	0.037	7.8	3.3
6	5 85	30.0	0.054	8.1	3.0
7	4.4	45.9	0.071	8.5	4.0
8	3.35	64.0	0.081	8.2	3.9
9	2.6	79.5	0.093	7.7	3.7
10	1.9	100.0	0 101	7.5	3 7
				7.1	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	$k_1 \times 10^2$	$k_4 \times 10^2$
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	0.191	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	191.0	0 031	4 6	2.18
				Average	2.09

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 in 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	0.0843	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 2¼ times as great as in those of Table XIII.; if the rate is inversely proportional to the concentration of the acid then

$$k_1 (\text{Table XIV.}) = \tfrac{1}{9} \text{ of } k_1 (\text{Table XIII.}) = 20 \times 10^{-4}.$$

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

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

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_4 in Table XIV.; but its value at the beginning of the experiment (line 1, Table XIV., $k_4 = 5 \times 10^{-4}$) 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 measurable 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; 0.6

No.	Reading	n	t	$k_4 \times 10^4$
1	41.6	0.0	0.0	—
2	41.0	1.83	0.007	4.92
3	39.25	1.83	0.029	7.01
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	7.61
8	25.45	62.5	0.191	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	7.61
			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 3.

Temperature coefficient

The experiments of Table XVI. were carried out at 10^2 C, all the others at 0° C. By comparing the values of k from Tables XVI. and XVII., it will be seen that a rise in temperature of 10^2 C multiplies the **rate by 3.39.**

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	$k_1 \times 10^2$
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	0 119	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	2.11
9	5 85	59.3	0 0631	2.62
10	3 9	78.5	0 0423	2 81
11	3 0	95 3	0 0325	2 82
12	2.9	123.0	0 0314	2.20
			Average	2.51

Resume of Tables I XVI.

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

k_1 has been taken from line 1 of each table. k_1 is the average of all the values (except the first) in each table, and k_3 has been calculated from k_1 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	A	$k_1 \times 10^2$	$k_2 \times 10^2$	k_3
I.	0.216	2 17	1 56	2 73	0 6	2.15	5 7	0.26
II.	0 216	1.95	1.56	2 71	0 6	1.25	6 4	0 29
III.	0 216	2 17	5 95	2 71	0 6	0.15	5 4	0 25
IV.	0 216	2 17	1 56	5 17	0 6	1 25	3 0	0.28
V.	0 216	2 17	1 56	8 20	0 6	0.88	2 4	0 29
VI.	0 190	4 95	2 44	5 17	0 6	0 68	3.2	0 29
VII.	0.216	4 95	3 02	5 47	0 6	0.76	3.5	0.32
VIII.	2 35	0.217	3 01	8 20	0 6	2 32	2 2	0.30
IX.	4 92	0.217	2 99	8 20	0 6	1 4	2 0	0 28
X.	2 46	0.217	2 99	8 87	0 6	5 8	4 2	0.27
XI.	1 22	0 121	1 50	4 19	0 6	7 8	3 6	0.25
XII.	2 46	0.217	2 01	8 20	0 6	6 4	2 4	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	0 199	0 500	22 75	0 6		0 75	0 28
XVI.	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 IODINE

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_3 defined as follows:

$$ k_3 = \frac{dx}{dt} \cdot kA \quad C \quad D \quad (E - x). $$

Temperature 16 C. All the others, o 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 quan-

rity 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	n	x	C—x	$k_1 \times 10^3$	$k_3 \times 10^6$
.	0 0	0.0	0 0	0.1385		
2	4 0	1.2	.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	1.97
5	15.2	10 5	0.0361	0.102	10 8	1.85
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	0.0618	0.0737	6.6	1.30

58.3 cc sodium thiosulphate solution is equivalent to 0.1385 units I_2.

TABLE XIX.

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

No.	Reading	n	x	C—x	$k_1 \times 10^3$	$k_3 \times 10^6$
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 8.
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_2.

TABLE XX.

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

No.	Reading	θ	t	E x	$k_1 \times 10^5$
1	0.0	0.0	0 0	0.290	
2	3.45	2.7	0 0224	0 268	
3	11.65	10.8	0 0757	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 1	108 0	0.269	0 024	10 5

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

TABLE XXI.

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

No.	Reading	θ	t	E x	$k_1 \times 10^5$	$k_2 \times 10^2$
1	0.0	0 0	0 0	0 290		
2	1 7	2 2	0 0109	0.279		
3	7 55	12 8	0 586	0.211	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	0 141	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 51	9 34
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.

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TABLE XXII.

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

No.	Reading	n	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	3.3	0.0146	0.122	
4	12.5	10.3	0.0469	0.090	6.3
5	18.1	17.0	0.0666	0.069	17.4
6	25.1	28.5	0.0923	0.044	17.2
7	30.3	42.2	0.1114	0.025	17.3
8	32.8	53.2	0.1206	0.015	17.5
					17.7

35.0 cc sodium thiosulphate solution is equivalent to 0.136 units I.

TABLE XXIII.

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

No.	Reading	n	t	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	0.0611	0.075	7.32
6	20.1	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	3.81

35.0 cc sodium thiosulphate solution is equivalent to 0.136 units I.

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 per cent 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 Table XXIII. and XIX. the rate seems to fall

TABLE XXIV.

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

No.	Reading	n	x	$E-x$	$k_1 \times 10^3$
1	0.0	0.0	0.0	0.290	
2	2.85	2.5	0.0485	0.274	
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	0.1116	0.171	9.77
6	21.8	29.3	0.112	0.148	9.84
7	25.2	37.0	0.163	0.126	9.65
8	29.9	47.3	0.191	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_2.

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	n	$k_1 \times 16$
1	0.0	0.0	
2	3.35	2.3	
3	7.05	5.7	9.4
4	12.0	12.5	10.0
5	.5	17.3	10.1
6		22.7	9.1
7		28.5	10.0
8		35.0	10.1
9	0	44.3	10.0
10	0	54.3	9.9
11	34.0	67.0	9.7

44.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_2.

TABLE XXV.

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

No.	Reading	n	r	E - x	$k_1 \times 10^3$
1	0.0	0 0	0.0	0.290	—
2	1.5		0.00975	0.280	—
3	4.7	8.0	0.0307	0.259	5.22
4	7.7	11.8	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	0.108	0.108	4.69
11	32.1	119.0	0.182	0.082	4.50
12	36.2	160.0	0.235	0.055	4.47

41.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_2.

TABLE XXVI.

C. 1.88; D. 9 15; E. 0.290; V 0.13

No.	Reading	n	r	E - x	$k_1 \times 10^4$
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 01
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 05
11	29 3	223 0	0 191	0.099	2 06
12	32 7	279 0	0 212	0 078	2 02

41.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_2.

TABLE XXVII.

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

No.	Reading	θ	x	$E-x$	$k_1 \times 10^6$
1	6.0	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	7.1	44.5	0.0482	0.242	1.78
5	11.05	68.0	0.0719	0.218	1.76
6	15.5	101.5	0.1007	0.189	1.72
7	19.1	139.0	0.124	0.166	1.71
8	22.4	175.0	0.146	0.114	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

41.6 cc sodium thiosulphate solution is equivalent to 0.290 units I.

TABLE XXVIII.

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

No.	Reading	θ	x	$E-x$	$k_3 \times 10$	$k_1 \times 10^4$
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	71.0	0.0122	0.298	4.22	2.51
5	9.15	296.0	0.0131	0.267	3.62	2.17
6	24.6	991.0	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	n	x	E - x	$k_2 \times 10$	$k_1 \times 10^4$
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	0.301	3.51	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	0.590
				Average	2.88	

65.5 cc sodium thiosulphate solution is equivalent to 0.310 units I_2.

Table XXX.

C. 1 88; D. 18 75; E. 0 290; V. 0.26

No.	Reading	n	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 12
6	9 4	99 8	0 0611	0.229	9 61
7	11 6	131 0	0 0745	0 215	9 45
8	11 4	176 0	0 0936	0 196	9.31
9	15 9	197 0	0.1034	0 187	9 33

41.6 cc sodium thiosulphate solution is equivalent to 0.290 units I_2.

off more rapidly than the concentration of the iodine — at least, the "constant" k_2 calculated on the assumption that the rate is proportional to the concentrations of the iodine 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 triiodion; 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

$$H \, AsO_3 + IOH = AsO_4 + I + 2 \overset{+}{I}.$$

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 9H: D. 11 7: E. 1.16: V. 0.12

Temperature 10° C

No.	Reading	a	x	$k_1 \times 10$
1	0 0	0 0	0 00	
2	2 9	1 7	0.0316	
3	6 2	4.2	0 0676	4.9
1	8 5	6.5	0 0926	8.8
4	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	*n*	*x*	$k_3 \times 10^7$
1	0.0	0.0	0.0	
2	2 85	8 5	0 0408	
3	1 6	15.8	0 0658	
4	6 3	23 0	0 0905	1 5
5	8 9	35 0	0 127	3.6
6	10 8	48.3	0.155	3 2
7	12 7	63.8	0.182	2.9
8	14 7	81 8	0 210	3.6
9	18.8	111.0	0.269	2.8
				2.9
			Average	3.1

1 cc sodium thiosulphate solution is equivalent to 0.0113 units i_3.

Temperature coefficient.

Comparing Tables XXXI. and XXXII., it appears that a rise of 10° C multiplies the rate by 2.3.

PART III.

EQUILIBRIUM.

A priori considerations, and the results of some preliminary experiments made it seem probable that at equilibrium the relation [1]

$$K_e V^6 = \frac{(E + x)(D + x)^2 (C + x)^3}{(A - x)(B - x)} \qquad \text{Eq. 8.}$$

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 constituents

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[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.

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 330), 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 the sulphate in quantity sufficient to remove almost all the triiodion, in so far as 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 38[1], 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 bottles[1] in which the concentration of the triiodion was twice that of the standard, while the concentration of the iodion was $\sqrt{2}$, $\sqrt[3]{2}$,

and $\sqrt[3]{2}$ 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_a (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

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

Series A (page 353), that multiplying the concentration of the iodion by four divided k_1 by fourteen instead of by sixteen.

TABLE XXXIII.

No.	A	B r	C + r	D + r	E + r	V	$K_4 \times 10-$
1	0.01857	0.3124	0.5689	1.440	0.4046 0.1		15.1
2	0.03607	0.3432	0.5750	1.512	0.4008 0.1		16.1
3	0.03098	0.3381	0.5804	1.446	0.4059 0.1		15.8
4	0.04792	0.3260	0.7958	1.427	0.3800 0.4		14.2
5	0.0754	0.3452	0.7198	1.437	0.3988 0.4		14.6
6	0. 16	0.3411	0.6856	1.444	0.4029 0.4		14.8
7	0.03941	0.3465	0.5717	1.436	0.801 0.4		14.1
8	0.03509	0.4720	0.5760	1.138	0.4018 0.4		16.5
9	0.01635	0.1699	0.5742	1.139	0.4039 0.1189		17.7
10	0.0198	0.1734	0.5677	1.156	0.4004 0.1449		16.1
11	0.0212	0.1748	0.5663	1.135	0.3990 0.1423		15.8
12	0.04903	0.3428	0.5685	1.439	0.4012 0.1		14.6
13	0.01113	0.3349	0.5652	1.447	0.4094 0.1		26.1
14	0.01787	0.3412	0.5596	1.430	0.4023 0.1		14.8
15	0.04646	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 r	C + r	D + r	E + x	V
1	0.0384	0.0384	0.4836	0.1991	40.80	0.0985	0.1
2	0.0768	0.0909	0.5036	0.1804	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 acid was de-

[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.

pendent on the concentration of the sulphuric acid (Series D), I under-
took 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 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_1/k_2 by 1.6, which is not far from
1.4, the square root of 2.

Relation between k_1, k_2, and K_0

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

$$K_0 = \frac{k_1}{k_2}.$$

Introducing the values $k_1 = 0.28$ (Table XVII.), and $k_2 = 3.26$
$\times 10^{-5}$ (Table XXXIII.) gives 8.6×10^{3} as the "calculated" value
of K_0; while direct experiment (Table XXXIII.) gives $K_0 = 1.5 \times 10^{5}$.
The two numbers are thus of the same order of magnitude.

In selecting k_2 I was forced to use the data of Table XXVIII., 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_1, k_2, and K_0 is due in part to this circumstance.

CONCLUSION

The results of my experiments can only be regarded as a very strik-
ing 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 scheme[1]

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

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,

$$-dx/d\theta = k'.x.y.z,$$
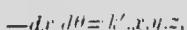
but if the concentration of the iodide or of the acid be increased, higher
powers of y and z must be introduced into the equation.

Finally, in Part III. it is shown that the condition of equilibrium
of Eq. 1

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

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 pro-
portion 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 solu-
tions 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 394 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 experi-
ments carried out at higher temperatures show that the temperature co-
efficient of the equilibrium constant accords, both in sign and in magni-

[1] Using the symbols of page 367.
[2] In the experiments of Table XX it is of the fifth order.

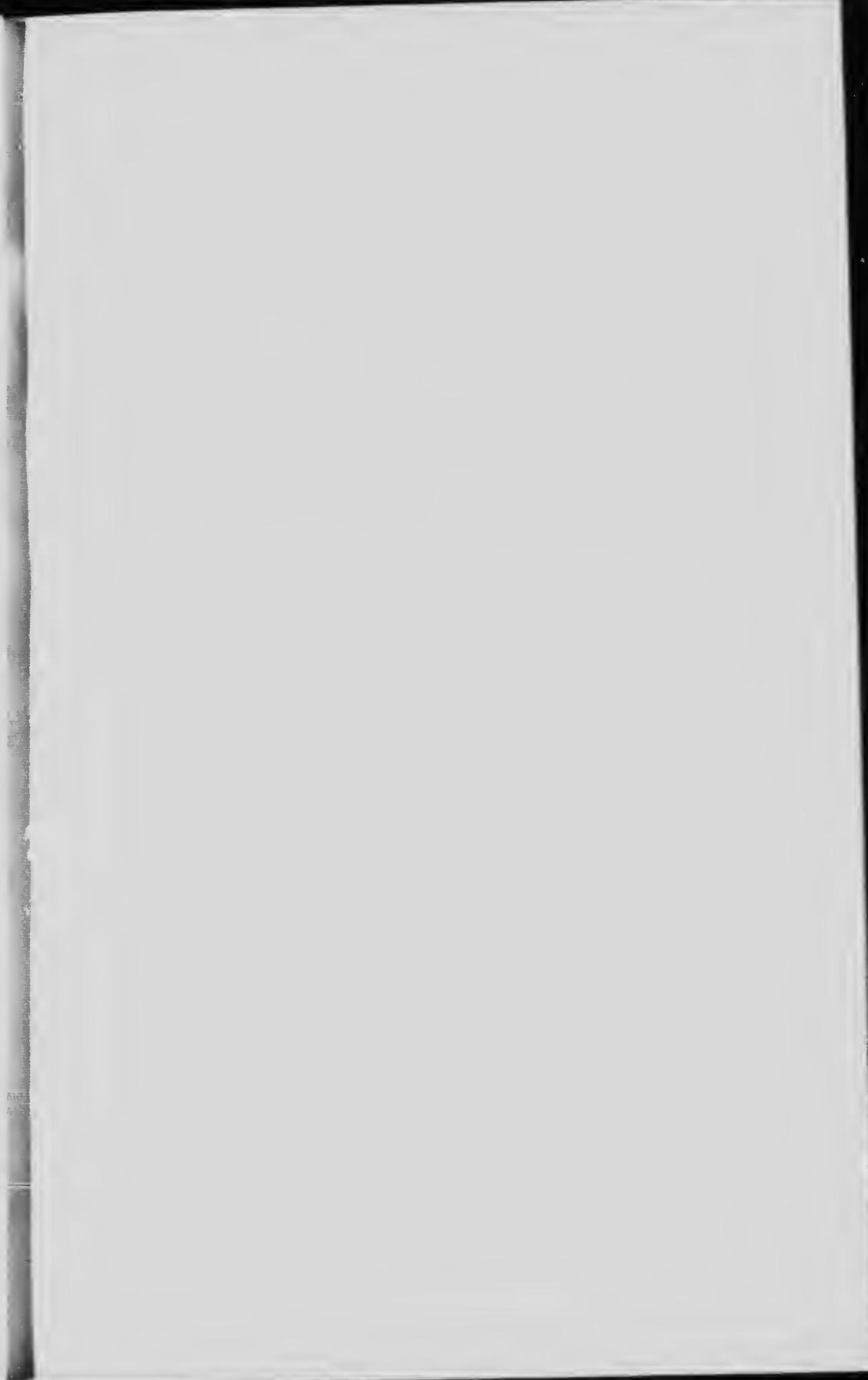tude, with the quotient of the temperature coefficients of the two rates (page 396). Owing to the conditions under which the measurements were carried out, a closer agreement could hardly be expected.

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.

TABLE OF CONTENTS.

THE RATE OF THE REACTION BETWEEN ARSE-NIOUS ACID AND IODINE IN ACID SOLUTION; THE RATE OF THE REVERSE REAC-TION; AND THE EQUILIB-RIUM BETWEEN THEM

(SECOND PAPER)

BY J. R. ROEBUCK

In a former paper,[1] the rate of the reaction between arsenious acid and iodine in a solution containing potassium iodide and sulphuric acid was found to be in close agreement with the formula

$$d\lambda\,d\theta \quad K \quad \frac{\text{(Iodine) (Arsenious acid)}}{\text{(Sulphuric acid) (Pot. iodide)}^2} \qquad (1)$$

and the assumption of an hypothetical intermediate product (HIO) in the reaction, served to connect this expression with the equation for the chemical reaction. Except in a single experiment (Table 14, page 379) all of the substances behaved normally; i. e., obeyed the Mass Law without modifying assumptions.

In the reverse reaction, i. e., the reduction of arsenic acid by potassium iodide in the presence of sulphuric acid, the rate was found to be expressed by the formula

$$dv\,d\theta \quad K \text{ (Arsenic acid) (Pot. iodide)}^a \text{ (Sulphuric acid)}^b \qquad (2)$$

where, in the solutions used, the numbers a and b were greater than unity but as far as could be inferred approaching unity for dilute solutions. Unfortunately this reaction does not take place in strongly diluted solutions,[2] the equilibrium in such solutions lying practically to the right in the equation

$$\text{H}_3\text{AsO}_4 \quad \text{HIO} \quad \text{H}_3\text{AsO}_3 + \text{H} \quad \text{I.} \qquad (A)$$
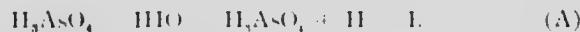
[1] Jour. Phys. Chem., **6**, 365 (1902).

[2] Zeit. phys. Chem., **47**, 121 (1904). The reviewer suggests using only dilute solutions.

The measurements show that the rate to the right is about 100,000 times that to the left.

The equilibrium condition was found to be fairly well expressed by the formula

$$K \quad \frac{(\text{Pot. iodide})' (\text{Sulphuric acid})^2 (\text{Arsenic acid})}{(\text{Iodine}) (\text{Arsenious acid})} \qquad (3)$$

and each constituent, in moderately dilute solution, was proved to have indices close to these. In more concentrated solution the same abnormal action of the acid was demonstrated.

Considering the important bearing of the data upon the Theory of Kinetic Equilibrium, better agreement between the calculated and observed Equilibrium Constants was much to be desired; and it was hoped that further experiments would show the cause of the discrepancy. The abnormal action of the potassium iodide and sulphuric acid required further study. Substitution of hydriodic acid for the sulphuric acid in both rates simplifies the considerations. With these objects in view several series of experiments were carried out.

The methods are, in general, identical with those employed in the previous work. The Units and Symbols are also the same; namely, A 1 tri-iodion iodine dissolved in a solution of potassium iodide of which latter an excess was always present and was allowed for in calculating C in the reacting mixtures; B arsenious acid white oxide of arsenic dissolved in sodium carbonate solution, which was made acid by the sulphuric or the hydriodic acid in the reacting mixture;

C I iodide ion, assuming complete dissociation of both potassium iodide and hydriodic acid but the iodide ions necessary to form tri-iodion with the free iodine are not included in

C; D H the acid (hydrogen) ion and in the experiments the amount necessary to neutralize the carbonate and the arsenite in B is always deducted; E arsenic acid. The units of mass are 1 100 of the quantities, in grams, in the equation

$$H_3AsO_4 \quad I \quad H_2O \quad H AsO_4 \quad (3I) \quad (2H) \qquad (B)$$
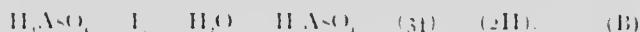
The unit of time is one minute and the unit of volume is one liter. Except when otherwise stated, the experiments were all carried out at o° C. For convenience of reference the rate to the right in above equation (B) is spoken of as the "Direct Rate" and the rate to the left as the "Reverse Rate."

PART I. EXPERIMENTS USING SULPHURIC ACID
Series A.—Extended reverse rate measurements

In the reduction of arsenic acid by potassium iodide and sulphuric acid, it was observed in the former paper that the latter constituents seemed to not obey the mass law and to require variable values for a and b in Equation 2 above. To find the extent of this abnormal action, advantage was taken of the fact that increase of either of these constituents accelerates the rate. Consequently by alternately doubling the one and halving the other, the experiments were made to cover practically the whole possible concentration of the two constituents, still keeping the velocity of the rate within limits allowing of easy measurement. At the same time the concentration of the arsenic acid was always much less than the smaller of the other two concentrations, so that in a first approximation the velocity of the rate was affected only by changes in the concentration of the arsenic acid. That is, in the general formula

$$d x/dt = K (C - x) (D - x) (E - x)V^2 \qquad (4)$$

C and D are always large compared with E and therefore always still larger compared with x. Thus the expression (4) becomes practically

$$d x/dt = K CDV^2 (E - x) \qquad (5)$$

of which the integrated form is

$$K_1 t = Log_{10}(E - x) \qquad (6)$$

where

$$K_1 = K CDV^2 \cdot 0.434. \qquad (7)$$

The reactions were carried out in suitable sized flasks kept at o° C by immersion in a well-stirred bath of snow and water. The solution for the reaction was prepared in two parts which

were cooled to o C before mixing. In one flask the potassium iodide was mixed with part of the sulphuric acid and part of the water; in the other flask the arsenic acid was mixed with the remaining sulphuric acid and water. By thus dividing the sulphuric acid to about the same concentration in each flask, no rise in temperature took place when the contents of the flasks were mixed and the reaction commenced. To allow for iodine set free during cooling by oxygen dissolved in the acid potassium iodide solution, proportional parts of each cooled mixture were measured out before starting the reaction, added one after the other to several times their volume of cold distilled water, and the free iodine determined. This reading, which was always proportionally very small (averaging about half a cubic centimeter), was subtracted throughout from the total reading and the difference recorded in the Tables.

The progress of the reaction was determined at intervals by measuring out usually 10 cc of the reacting mixture with a cold pipette into a cold beaker, diluting with ice-water to stop the reaction and reduce the concentration of the acid, and then quickly titrating with sodium thiosulphate solution. On account of the oxidation of the sodium thiosulphate by the arsenic acid, care was taken never to add more than a slight excess of the former during titration. In case the reaction had proceeded to any extent or was a very slow one, it was found necessary to add with the cold diluting water, sodium thiosulphate solution in quantity almost sufficient to decolorize the part of the mixture taken for titration, and finishing the addition of sodium thiosulphate solution as quickly as possible. If this precaution was neglected, the reaction of the Direct Rate, accelerated by the dilution, would introduce a serious error into the reading.

At the head of each table is given the initial quantities of each of the reacting substances and the volume in liters of the mixture. Under "Reading" is given the sodium thiosulphate titration obtained as described above. Under θ is given the interval in minutes from the time of mixing the two parts to start the reaction, to the time of diluting the part taken for titration. At the foot of the table is given the reading corresponding to

the total possible amount of iodine set free by the arsenic acid
in the part taken for titration. The values of r are calculated
by the proportionality between this final reading (where $E = x$)
and the reading at the time in question. Under K_1 is given the
value calculated by Equation (6); throughout the time of the
first reading and not the time of mixing is used as zero time in
the calculation, thus avoiding the irregular reaction during the
time of mixing. This choice of zero time required the use of
$(E - r)$ from line one as the initial E; C and D were usually
so large that the difference was negligible. In Tables 1, 4, 9,
and 10, K is calculated from the integral of Equation (4) assuming
only D (or C) constant.

Tables 1–10 were carried out according to the plan out-
lined above (page 729). The results of these and other experi-
ments are summarized in Table 20. The factor by which K_1 in-
creases for multiplying D by 2 at the concentrations in question
is given under "D factor," and the similar number for C under "C
factor." Under "D index" and "C index" is given the value required
for b and for a in Equation 2 in order to give the corresponding
factor. As will be seen, the numbers increase very rapidly in
both cases with increase in concentration. In case of the sul-
phuric acid (D), where the limits of concentration are wider,
the index goes from 1 to 3.7. In Tables 11 and 12 the index
has fallen to 1 and from the way in which it falls off this would
appear to be the lower limit and to hold for solutions where
none of the reacting substances are present in greater concentra-
tion than 3 Units per 120 cc. In the case of the iodide (C) the
index is approaching 1 in Tables 1 and 2, and probably is 1 in
Tables 11 and 12 where, therefore, the general formula (Equa-
tion 1) with all indices unity holds. Consequently $K = 3.9$
10^{-7} calculated from these tables increases in each of the pre-
ceding tables with the increase in C and D but parallel also
with the increase in $d\tau/d\theta$.

Dividing the constant $1.2 \cdot 10^{-6}$ of Table 2 by the successive
D factors 5.4, 3.3, 2.9, 2.6, and calculating the value of K, as-
suming this the value of K where $D = 1.21$ and $C = 1.36$
gives $2.16 \cdot 10^{-7}$. Taking the constant $0.76 \cdot 10^{-7}$ of Table 9 and

treating it similarly gives K_3 = 2.23 10⁻?. This value is only about half that in Tables 11 and 12. Also the D factors in the pairs of experiments 11–12 and 9–10 are quite different. It will appear later that K_1 is probably a function of $dx/d\theta$ to which these peculiar results may be due. Failing such an explanation, it would appear that the constituents are not independent in their action on the rate but are influenced by the presence of other constituents.

In my former paper it was assumed that under the conditions of measurement the effect of the reaction opposite to the one being measured, could be safely neglected. This assumption was completely justified in the measurements of the Direct Rate as also in the greater part of the Reverse Rate measurements. In a few experiments (for example, Tables 23 and 24a of the former paper) the constant shows a falling off at the last reading where the rate is carried to almost complete disappearance of arsenic acid. This may also be observed in some of the tables of the present paper, but where this error extended further than the end measurements, a correction has been made. In taking averages where the last values show a decrease they are omitted.

In Tables 28 and 29 of my former paper, the reverse rate measured was very slow, the direct rate constant is about 10' greater, and consequently this error is here not negligible. For the purpose of correction, Tables 28 and 29 of the former paper are produced here as Tables 11 and 12. The suggestion as well as the method of correction I owe to Mr. W. C. Bray.[1] In Tables 11 and 12, K_1' is calculated by Equation (6) but using pairs of consecutive values of (E — 1) and the difference between the corresponding values of θ. This method magnifies the experimental errors but is to be preferred as emphasizing also any regular variation in the constant. The actually measured rate R is calculated by supplying the values in

$$R = dx/d\theta = 2.30 \, K_1' \, (E - 1). \tag{8}$$

The direct rate is calculated by the equation

$$R_1 = 0.28 \times V \cdot C - x)^2(D - 1). \tag{9}$$

Jour. Phys. Chem., 9, 573 1905.

and the corrected value of K_1' is given by

$$K_1'' \quad K_1' \frac{(R + R_1)}{R}. \qquad (10)$$

It will be observed that the corrected constant K_1'' shows a regular and pronounced increase.

This increase of the constant might be due to catalysis by a product of the reaction. To test this the experiments of Tables 13, 14, and 15 were carried out. Table 13 serves for comparison with 14 and 15. The experiment of Table 14 was made with an initial charge of tri-iodion and of Table 15 with one of arsenious acid. The value of K, and the course of the reaction in all three tables are identical, proving conclusively the absence of any catalysis by these, the only known products of the reaction. Similar experiments at greater concentration of both potassium iodide and sulphuric acid gave the same result.

This increase of the reverse rate constant as the reaction neared equilibrium gave a variation of the kind required for better agreement between the calculated and observed values of K_c. To test the quantitative sufficiency, it was necessary to follow a rate right up to equilibrium. To simplify the considerations C and D should be much greater than A, B, and E, at any time during the reaction. The direct rate should be treated similarly and to this end the equilibrium should be reached with about half the possible amount of tri-iodion. Hence the equilibrium formula

$$K_a \quad \frac{(C - 1)^3 (D - 1)^2 (E - 1)}{(A - 1)(B - 1) V^4} \qquad (11)$$

was solved for A using K, 1.5 10 and 10A 10B C D E 201 and V 0.50. To obtain identical conditions in the reacting mixtures it was necessary to make both direct and reverse rate mixtures from the same reagents, which was accomplished as follows. The reacting mixtures of Tables 16 and 21 were made up from identical quantities of the solutions of tri-iodion (A), arsenious acid (B), potassium iodide (C), and sulphuric acid (D). In Table 21, A with a little water was cooled

in one flask and the remaining constituents and water in a second flask. The two parts were mixed to start the reaction which consequently took place with disappearance of tri-iodion and gave a measurement of the direct rate. In Table 16, the two parts were made up differently : C and D were mixed with half the water in one flask and A and B with the remaining water in the other. Consequently in the latter flask the reaction between A and B took place quickly and by the time all were at 0° C, the solution was only slightly colored, almost all A and B having disappeared. On mixing these two parts the reaction took place with the separation of tri-iodion and gave a measurement of the reverse rate.

The reacting mixtures of Tables 17 and 22, were made up from identical quantities of the solutions of potassium iodide (C), sulphuric acid (D), and arsenic acid (E), all being so chosen as to give the same equilibrium mixture as in Tables 16 and 21. In Table 17 the potassium iodide, half the sulphuric acid, and half the water were cooled in one flask, while the arsenic acid with the remaining sulphuric acid and water were cooled in the other. The two parts were mixed to start the reaction which, therefore, took place with the separation of tri-iodion and gave a measurement of the reverse rate. In Table 22, all three constituents were mixed with only sufficient water to keep all in solution while the balance of the water was cooled in a second flask. A quick reaction immediately took place between the three constituents, so that by the time all were at 0° C, almost all the arsenic acid had been reduced to arsenious acid. On mixing with the remaining water, a reaction took place with the disappearance of tri-iodion and gave a measurement of the direct rate. So that these four experiments gave a measurement of each rate with each set of reagents and also a measurement of the equilibrium from each side with each set of reagents. The reactions were very slow, lasting almost a week. To avoid as far as possible the oxidizing action of the air, the solutions were kept in 100 cc glass-stoppered bottles, and 25 cc were taken for each titration. The sodium thiosulphate solution changed

slowly during this interval and its strength was regularly checked by a stronger solution of iodine kept away from strong light. This correction on the last day amounted to about ¼ percent The readings recorded in the tables are corrected for this change in the thiosulphate solution.

Tables 16 and 17 are the two reverse rate measurements. In both the course of the reaction and the equilibrium readings are practically identical. The solutions used to make up the reacting mixture of Table 17 involved the formation of considerable sodium sulphate which, therefore, has no appreciable effect on the course of the reverse rate; neither is there a small quantity of any other material in one mixture only, affecting the course of the reverse rate. The columns headed K_1, K', R, R_1, K_1 calculated as shown above from Equations (6), (8), (9), and   It will be observed that K' shows a more rapid decrease approaching equilibrium than does K_1. K''_1, the corrected value of K', shows a regular increase as was also the case in Tables 11 and 12. K'_2 of Table 11, the slower of the two latter Tables, has the greater final value and this value is somewhat less than the initial values in Tables 16 and 17. It must therefore be concluded that at equilibrium, in dilute solutions at least, K'_2 2.0 10⁻⁵.

Under "M" in Table 16 is given the value of the constant calculated from

$$ dx/dt \quad M(E - x)^2 \quad K''_1(E - x) \qquad 12 $$

in which it is assumed that the arsenic acid acts according to the second power. The tabulated values show a much greater variation than K''_1. In these experiments C and D are practically non-variant and it must either be assumed that the arsenic acid $(E - x)$ acts according to a fractional power or that the constant depends on $dx/d\theta$. To make the constant non-variant requires different fractional indices for $(E - x)$ in the different experiments—for example, the experiment of Table 20 (page 385) of former paper has a 10 percent variation of K_1 for a 90 percent variation of $(E - x)$ and the index in this case would be almost unity. It seems simpler to say that K is an inverse function of dx/dt. This is supported by the fact that the fast

rates give K', almost constant but when R, is small they show
an increase. It offers a satisfactory escape from the conclusion
noted on page 732 of the lack of independence of the constitu-
ents. It supplies a good reason for the small values of K, in
Tables 2–13. The increased value in Table 1 may safely be at-
tributed to the divergence of the sulphuric acid from the simple
laws when in concentrated solution (4.8 normal). It must also
be observed that in the direct rate measurements (Table 14, page
379, of former paper) the sulphuric acid increases its action
faster than its concentration when 2.0 normal but its action is
still proportional to its concentration when 0.03 normal.

Such a relation may be explained theoretically by the as-
sumption of a reaction in two steps neither of which is instanta-
neous. This possibility has been discussed[1] theoretically in sev-
eral papers but I am not aware of any practical application. The
equilibrium of the first step is not quite attained while the re-
action of the second step is removing one or more of the products
of the first, or conversely. In this case some hints may be ob-
tained as to the probable steps. First, no product of the reaction
retards the reverse rate so that the first step must be one of ad-
dition or at least one that does not produce either of the products
of the final reaction. Second, the rôle, normal and abnormal,
of the potassium iodide and the sulphuric acid are very similar
so that they probably play similar parts in both steps; this is con-
firmed when hydriodic acid is substituted for potassium iodide
and sulphuric acid. Third, arsenic acid must enter the first
step. The separation of a very small quantity of a crystalline
compound during some of the fast reverse rate measurements, is
in line with this hypothesis.[2] Consequently a probable first step is

$$HI + H_3AsO_4 = H_3AsO_4HI \qquad (C)$$

where water may be also split off. The second step could then be

$$H_3AsO_4HI = H_3AsO_3 + HIO \qquad (D)$$

To supply the desired explanation it is only necessary that the

[1] Bancroft: Jour. Phys. Chem. 4, 7 , (1900); Mittasch: Zeit. phys.
Chem., 40, 1 (1902); Jungius: Zeit. phys. Chem., 49, 368 (1911)
[2] Quantity too small for analysis

reaction of equation (C) be of a measurable velocity when the velocity of the second step will be lessened by the decrease in the amount of the first step product and the second rate constant appear to depend on $dt\ d\theta$.

Mathematical treatment of the figures on this assumption is involved and does not seem to offer results worth printing. It would require the determination by algebraic means of at least two independent constants, the rate constants of the two steps, and could hardly fail to make a correction satisfactory enough to come within the large experimental error of such work. In case the amount of the intermediate product is small compared with r, the equilibrium function derived from this theory reduces to the form (equation 6) employed in the calculations. Also from the peculiar form of the first step, it is apparently without a point for experimental attack. The temperature coefficients are throughout in excellent agreement as would be predicted from this hypothesis. In fact it offers an excellent qualitative (and probably quantitative) explanation of all the irregularities except the increase of K in Table 1 which is very well accounted for by other means. I have not been able to form any explanation based on electrolytic dissociation which offers at all a satisfactory correlation of these peculiarities.

Temperature Coefficient.—The experiments of Tables 18 and 19 were carried out at 10 C. and the change of K, gives 2.37 as coefficient for this temperature interval.

Series B.   Direct rate near equilibrium

In the first paper the agreement between the mathematical expression for the direct rate and the experimental data left nothing to be desired. The experiments, however, did not cover the rate near equilibrium, which became advisable in view of the peculiar form of the reverse rate and of the lack of agreement with the equilibrium formula. The experiments of Tables 21 and 22 were carried out to test the constancy of K near equilibrium. On page 733 is given in detail the method of making the reacting mixtures and of following the course of the reaction. In the Tables K, is calculated from the integrated form of

$$R' \quad d\gamma \, d\theta \quad K_1 (\Lambda \quad \iota) \, 2.30. \tag{13}$$

and K_1' from this also, but using pairs of consecutive measurements. R_1 is calculated by supplying the values in Equation (13). R_2 is calculated from

$$R \quad K_1' \, 2.30 \, \iota \tag{14}$$

employing the equilibrium value of K_1' namely, $1.49 \, 10^{-4}$ of Table 16 for Table 21, and $1.55 \, 10^{-4}$ of Table 17 for Table 22. And K_1'' is given by

$$K_1'' \quad K_1' \frac{(R' \quad R_2)}{R'}. \tag{15}$$

The constant K_1'' shows no regular variation right up to equilibrium. The action of the air is shown in the last two measurements since only near equilibrium is it appreciable. That the increase of K_3 in Tables 16 and 17 is not due to this action of the air, is satisfactorily shown by the constancy of K_1'' which, were the other the case, would decrease. The average values of K in the two experiments are practically identical, namely, 0.260 and 0.262, and these fall within the values found in the first paper where the average was 0.28. The agreement of the two experiments shows as also in the case of the reverse rate, page 735, that the sodium sulphate has no effect on this rate and that there is no other substance present in small quantity in one of the mixtures only and affecting the direct rate. The constancy of K_1'' is also a very satisfactory proof of the accuracy of the method of correction since here the measurements go right to equilibrium.

Temperature Coefficient.—A pair of rates carried out at 10 C gave 0.86 for K at this temperature which agrees satisfactorily with the value of 0.95 of the former paper.

Series C. Equilibrium experiments

In the former determinations of Equilibria, the field covered was small and there was a possibility that the number found then for K was an accidental value. Unfortunately the field over which equilibrium determinations can be successfully made is not large. Arsenious acid can never be present in large quantity

on account of its slight solubility under these conditions. If arsenic acid is increased in the presence of much sulphuric acid and potassium iodide, beautiful spangle-like crystals separate. If potassium iodide and sulphuric acid are increased to any great extent, the equilibrium is reached with practical disappearance of arsenic acid which then has to be determined as the small difference between the total possible and the observed quantity of tri-iodion. Here also the oxidizing action of the air introduces a relatively large error, so that slightly more tri-iodion was occasionally found than could be accounted for by the arsenic acid initially present. It is almost impossible to exclude all the action of the air on hydriodic acid solutions which must stand for days, as in this case to allow the mixture to come to equilibrium.

The previous work having sufficiently demonstrated that false equilibria were not to be feared, the precaution of making the mixtures come to equilibrium from both sides was here given up. The mixtures were made up by measuring out the solutions with pipettes and making up the required volume with water. The mixtures were kept in full, well-stoppered bottles standing in the thermostat till, judging from past experience ample time had been allowed for them to come to equilibrium. Analyses were made exactly as described for slow reaction rates on page 73.

To test whether accidental conditions were disturbing the equilibrium, several mixtures were allowed to stand for three weeks at room temperature and after coming to equilibrium again at 25° a very slight increase in the tri-iodion was observed; this could easily be accounted for by oxidation by the air.

A number of experiments were made using carefully cooled solutions to which a trace of arsenic trioxide so that the action of the air was reduced to a minimum. These results were practically identical with those in which such precautions were neglected.

A large number of experiments were made in the first where they were practically at a temperature, set of given in Table

23. K_6 is calculated by Equation (11) and in no case did its value rise to 2.0 10^5. The true value probably lies between 1.0 and 1.5 10^5. It is quite probable that the variations in the value of K_6 are due to the experimental difficulty under which the determinations are carried out. The value of K_6 is obtained as the product of twelve experimental numbers, eight of which are determined by the value of the tri-iodion found by titration. This latter may be seriously altered by the action of the air. In concentrated solution of sulphuric acid, however, the value of K_6 will decrease on account of the increase in K_5 and decrease in K_3.

The value of the quotient $K_2 K_3$, using the equilibrium value of K_3 in Tables 16 and 17, is 1.3 10^5 while the value of K_6 from these experiments is 1.4 10^5; better agreement could only be a coincidence. The disagreement in the former paper is to be attributed to the small value of K, when $dx/d\theta$ is large.

Temperature Coefficient.—The experiments 10 and 11 of Table 23 were carried out at 10° C and give, by comparison with the other half of the same mixture kept at 0° C, a coefficient for this temperature interval of 1.41. The coefficient calculated from the rate coefficients is 1.43, and from the 20° C coefficient of the first paper is 1.34. So that these are in excellent agreement.

PART 2. EXPERIMENTS USING HYDRIODIC ACID

To complete the study of the reaction, it was necessary to carry out measurements, using hydriodic acid instead of sulphuric. Accordingly, a solution of hydriodic acid, about 6 mols. HI per litre, was made by the action of iodine on red phosphorus in the presence of water. The resulting solution of the acid was purified by several distillations in a current of hydrogen gas. In calculating C and D the hydriodic acid was treated as completely dissociated.

Employing the other solutions used in the previous work, three different series of experiments were carried out; Series D on the oxidation of arsenious acid by iodine in the presence of potassium iodide and hydriodic acid; Series E on the reduction

of arsenic acid by hydriodic acid solutions; and Series F, a set
of Equilibrium determinations.

Series D.—Direct rate in the presence of hydriodic acid

In making up the reacting mixtures and in carrying out
the rates the same methods were employed as are described in
the former paper where sulphuric acid was employed. The
method used for determining the effect of altering each constitu-
ent separately in the presence of one very small constituent, was
again employed. The formula found to hold in the case of sul-
phuric acid was again found true, *i. e.,*

$$dx/d\theta = K_3 \frac{(A - x)(B - x)V}{(C - x)(D + x)} \qquad (16)$$

and when B, C, and D are large compared with A (tri-iodion)
this becomes

$$dx/d\theta = K \frac{BV(A - x)}{C^2D} \qquad K_1 \cdot 2 \cdot 39 \quad A - x). \qquad (17)$$

Throughout A (tri-iodion) was the constituent present in small
quantity. The integrated form where only D is assumed con-
stant is also used and

$$K_t \quad K_1 V D. \qquad (18)$$

In Table 24 the constancy of K is sufficient evidence that
the first power of A is required in the formula and the same may
be observed in each of the succeeding tables. The value of K
should fall off slightly on account of the slight decrease in B,
C, and D; the larger decrease just at the end is due to the fact
that equilibrium is being approached.

In Table 25, while the other constituents are the same as in
Table 24, the iodide (C) is multiplied by the square root of 2;
K_1 falls to half its value in Table 24, showing that the iodide
acts inversely as its square.

In Table 27 the arsenious acid is half its concentration in
Table 24, and the value of K_1 falls to half; the arsenious acid
(B) acts therefore as its first power.

In Table 26, both C and D are varied but K_1, which is inde-
pendent of variations in A, B, and C, is double that of Table 24,

showing that the sulphuric acid (D) acts inversely as its first power. The relation between the values of K_1 in Tables 28 and 29 confirms this conclusion.

The results of the series are summarized in Table 30, where K_1 0.135 is constant well within the experimental error. This value is only half that found using sulphuric acid and the difference may be due to the greater dissociation of hydriodic acid.

Temperature Coefficient.—The experiments of Tables 28 and 29 were carried out at 10° C, and the relation of the constants gives 3.2 as the coefficient for this temperature interval; using sulphuric acid, the value was 3.39.

Series E. Reverse rate in the presence of hydriodic acid

In this series on the reduction of arsenic acid by hydriodic acid it was not possible to duplicate the extended set of rates of Series A, since the H ion could never be present in greater number than the I ion. The experiments of Tables 31–35 were carried out, using exactly the same procedure as in Series A, and the results are summarized in Table 37 where the headings have the same significance as in Table 20. The C factor and D factor are almost identical in both tables (20 and 37) for the same values of C and D—the divergence from the simple formula (Equation 4) is closely the same for C as for D. The value of K seems to be slightly larger than in the case of sulphuric acid.

Temperature Coefficient.—The experiment of Table 36 was carried out at 10 C and the value of K_1 gives, by comparison with that of Table 32, a coefficient of 2.53 for this temperature interval; the value for sulphuric acid was 2.37.

Series F. Equilibrium in the presence of hydriodic acid

In this series on equilibrium of mixtures with hydriodic acid, the same methods as are described in Series C were employed. A set of the determinations is given in Table 38. The value of K_1 for dilute solutions seems to lie in the neighborhood of 0.9 10. The value of $K_3 K_5$ from the results of Series D and E, is 2.5 10 so that about the same discrepancy is here observed as was found in the former paper in the work with sulphuric

acid.   From the analogy of the two cases there can be no doubt
but that experiments following this reverse rate to equilib-
rium would show the same excellent agreement as was finally
found in Series A.

Temperature Coefficient.—The experiments 11 to 14 were
carried out at 10° C and the other half of the same solution at
0° C.   The relation between the pairs of constants gives 1.25 as
the coefficient for this temperature interval ; the ratio of the rate
coefficients is 1.27, so that we have here again excellent agree-
ment.

Conclusion

The conclusions of the former paper receive the strongest
support from the more extended data recorded here.

The formula for the direct rate (Equation 16) is found to
hold with remarkable exactness for both sulphuric and hydriodic
acids and K_4 is non-variant right up to equilibrium.

The formula for the reverse rate (Equation 2) is found to
hold for very dilute solutions with a and b unity.   With in-
creasing concentration of iodide (C) and acid (D) the values of a
and b increase similarly.   The value of K_5 is found to increase
as the equilibrium is approached and also when the rate $dx/d\theta$ is
lessened by decreasing (E — r).   A satisfactory theoretical ex-
planation of these peculiarities is advanced.

The value of the equilibrium constant K_6 is $1.5 \cdot 10^7$—varia-
tions being possibly due to experimental errors.   This value is
in remarkable agreement with the quotient of the two rate con-
stants K_4/K_5 $1.4 \cdot 10^7$.   The ratio of the rate temperature coef-
ficients also shows the same excellent agreement with the
equilibrium temperature coefficient.   Finally, the peculiar action
of concentrated sulphuric acid, increasing its action faster than
its concentration, is shown in each of the rates and in the equilib-
rium.

In view of the complexity of both rates and equilibrium
functions, this application and confirmation of the Theory of
Kinetic Equilibrium must be regarded as the most satisfactory
known.

My thanks are due to Dr. R. F. Ruttan, in whose laboratory this work was carried out.

TABLE OF CONTENTS

TABLE 1

$\bar{1}$ (C), 1.358; H_2SO_4 (D), 28.92; H_3AsO_4 (E), 0.2835; V, 0.12

No.	Reading	θ	t	$E - t$	$K_1 \cdot 10^2$	$K_2 \cdot 10^6$
1	0.0	0.0	0.0000	0.2835	--	—
2	5.9	1.0	0.03186	0.2516	-	—
3	15.1	2.75	0.08154	0.2020	5.45	6.54
4	26.4	4.75	0.1425	0.1410	6.72	7.32
5	29.9	6.75	0.1615	0.1220	5.46	6.02
6	35.2	9.50	0.1900	0.0935	5.06	5.66
7	40.2	14.8	0.2171	0.0664	4.20	4.80
8	47.7	25.4	0.2576	0.0259	4.11	4.84
9	50.2	43.0	.2711	0.0124	3.12	3.72

Reading 52.5 is proportional to t　　0.2835

TABLE 2

1 (C), 1.358; H_2SO_4 (D), 19.28; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	t	$E - t$	$K_1 \cdot 10^2$	$K_2 \cdot 10^6$
1	0.00	0.0	0.0000	0.2835	.	
2	1.95	1.25	0.01053	0.2730	-	—
3	8.1	6.83	0.04574	0.2398	1.02	1.57
4	13.6	11.0	0.07342	0.2101	1.30	1.84
5	19.05	17.0	0.1029	0.1806	1.14	1.82
6	23.5	22.8	0.1269	0.1566	1.12	1.80
7	28.8	31.5	0.1555	0.1280	1.09	1.78
8	33.7	43.2	0.1820	0.1015	1.03	1.74
9	39.3	67.5	0.2122	0.0713	0.86	1.49

Reading 52.5 is proportional to t　　0.2835

TABLE 3

I (C), 2.716; H₂SO₄ (D), 19.28; H₃AsO₄ (E), 0.2835; V, 0.120

No.	Reading	t	x	E — x	K₁·10²
1	0.0	0.0	0.0000	0.2835	—
2	4.72	0.75	0.02548	0.2580	—
3	15.35	4.82	0.08279	0.2007	2.68
4	23.5	8.75	0.1269	0.1566	2.71
5	29.1	12.25	0.1571	0.1264	2.70
6	34.2	16.25	0.1847	0.0988	2.69
7	39.1	22.0	0.2111	0.0724	2.69
8	45.2	34.8	0.2441	0.0394	2.40

Reading 52.5 is proportional to x = 0.2835

TABLE 4

I (C), 2.716; H₂SO₄ (D), 9.64; H₃AsO₄ (E), 0.2835; V, 0.120

No.	Reading	t	x	E — x	K₁·10²
1	0.0	0.0	0.0000	0.2835	—
2	1.88	1.5	0.01015	0.2733	—
3	6.73	8.0	0.03625	0.2461	7.02
4	11.5	19.2	0.06210	0.2214	5.17
5	15.5	27.8	0.08370	0.1998	5.17
6	22.05	44.8	0.1191	0.1644	5.11
7	27.55	62.7	0.1487	0.1348	5.02
8	31.2	76.7	0.1685	0.1150	5.00
9	35.9	100.5	0.1938	0.0897	4.89

Reading 52.5 is proportional to x = 0.2835

TABLE 5

I (C), 5.43; H₂SO₄ (D), 9.64; H₃AsO₄ (E), 0.2835; V, 0.120

No.	Reading	t	x	E — x	K₁·10
1	0.0	0.0	0.0000	0.2835	
2	3.15	0.5	0.01701	0.2665	—
3	13.9	6.83	0.07505	0.2084	1.69
4	20.8	12.0	0.1125	0.1710	1.68
5	26.8	17.8	0.1447	0.1388	1.64
6	33.6	26.5	0.1814	0.1021	1.61
7	40.7	36.3	0.2198	0.0637	1.74
8	43.4	50.0	0.2343	0.0492	1.48

Reading 52.5 is proportional to x = 0.2835

TABLE 6
Ī (C), 5.432; H_2SO_4 (D), 4.82; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	r	E − x	$K_1.10^3$
1	0.0	0.0	0.0000	0.2835	--
2	2.55	4.25	0.01377	0.2697	
3	6.05	11.0	0.03267	0.2508	4.67
4	11.3	21.5	0.06103	0.2225	4.95
5	20.25	45.0	0.1215	0.1620	4.69
6	28.8	75.0	0.1555	0.1280	4.61
7	34.6	104.0	0.1868	0.0967	4.46
8	40.0	149.2	0.2106	0.0675	4.15

Reading 52.5 is proportional to x   0.2835

TABLE 7
Ī (C), 5.432; H_2SO_4 (D), 2.41; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	r	E − x	$K_1.10^3$	$K_1'.10^3$	$R.10^3$	$R_1.10^4$	$K_1''.10^3$	$K_1'.10^6$
1	0 0	0.0	0.0000	0.2835		—	—	—	—	—
2	0.68	1.5	0.00367	0.2798		—	—	—	—	—
3	1.9	8.0	0.01026	0.2732	1.85	1 85	—		1.85	0.56
4	5.4	26.5	0.02916	0.2543	1.67	1 1	—	—	1.90	0.58
5	11.85	64.2	0.06402	0.2195	1.68	1 5	—		1.65	0.51
6	17.25	101.0	0.09316	0.1903	1.69	.73	7.56	0.41	1.73	0.55
7	24.75	159	0.1336	0.1499	1.72	1.77	6.10	0.85	2.02	0.65
8	29 7	227	0.1604	0.1231	1.59	1.27	3.60	1.21	1.68	0.55
9	32.9	270	0.1776	0.1059	1.58	1.48	3.6.	1.50	2.10	0.69
10	37.0	340	0.1998	0.0837	1.55	1.47	2.64	1.89	2.58	0.86

Average 4–8   1.67

Reading 52.5 is proportional to x   0.2835

TABLE 8

$\overline{I}$ (C), 10.88; H_2SO_4 (D), 4.82; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	x	$E - x$	$K_1.10^7$
1	0.0	0.0	0.0000	0.2835	—
2	5.95	1.67	0.0277	0.2558	—
3	18.0	6.33	0.0837	0.1998	2.30
4	30.9	13.4	0.1372	0.1463	2.08
5	41.5	22.5	0.1930	0.0905	2.17
6	46.6	29.4	0.2162	0.0673	2.10
7	52.0	40.7	0.2418	0.0417	2.02
8	56.2	58.0	0.2613	0.0222	2.06
				Average 4–8	2.09

Reading 60.9 is proportional to x 0.2835

TABLE 9

$\overline{I}$ (C),   88; H_2SO_4 (D), 2.41; H_3AsO_4 (E), 0.2835; V, 0 120

No.	Reading	θ	t	$E - x$	$K_1 10^7$	$K_3.10^6$
1	0.0	0.0	0.0000	0.2835	—	—
2	1.1	1.0	0.00512	0.2784	—	—
3	6.05	6.17	0.02815	0.2554	5.73	1.14
4	14.7	16.2	0.07541	0.2081	8.29	1.28
5	22.2	27.5	0.1033	0.1802	7.13	1.10
6	29.8	42.0	0.1387	0.1448	6.91	1.07
7	38.2	64.8	0.1777	0.1058	6.57	1.01
8	42.9	82.0	0.1996	0.0839	6.43	1.02
9	46.6	100.5	0.2169	0.0666	6.27	1.00
				Average 4–6	7.44	

Reading 60.9 is proportional to x 0.2835
Correction for the direct rate is negligible

TABLE 10

$\bar{T}$ C°, 10.88 ; H SO$_4$ (D), 1 21 ; H$_3$AsO$_4$ (E), 0 2835 V, 0,120

N	Readin_	*a*	t	E t	K, 10	K 10⁵
1	0.0	0 0	0.00000	0.2835		
	0.7	1.17	0.00325	0 28··		
	2.35	5 5	0.01092	0.27··	2.82	0.68
4	·· 7	17 ·	0.03115	0 2524	2.81	0.84
	1,	·1 ,	0.0800	0.203·	2.76	0.84
6	· · ·	·· 5	0.0053	0.18·2	2.64	0.83
·	···	·8,8	0.11·1	0.16·4	2.59	0.82
·	·	110,0	0.1371	0.1404	2.56	0.82
9	· ·	137 0	0 154·	0.128·	2 45	0.80
10		160	0.1674	0.1161	2 39	0.78

Average   4–8   2.67

Reading 60.0 is proportional to v   0 2835

TABLE 11

Table 28 of First Paper

$\bar{T}$ (C   2 27·; H SO$_4$ (D·, 2 ·03 ; H AsO$_4$ (E), 0 310 ; V, 0,155

No	Read ing	*a*	t	E	K	K'/10⁴	R 10⁴	R 10⁴	K'/10⁴ K'	10⁵
1	0 0	0,0	0,0000	0 310	—	—		—		
2	0 35	10 0	0,00161	0 30·		—		—		
3	2 3	60 0	0,0107	·0 29·	2 30	2.30	·58	—	2 30	0 38
4	2 65	74 0	0,0122	·· ·9·8	2.51	2.53	1 73		53	· 42
5	54	20,6·	0,0434	0 ·7	2 17	2.16	1 33	0 073	27	· 39
6	21 6	9,4	0 11·	· 1·7	1 ·7	1.88	·8··0,546	··9	·· 56	
7	26,6	11·77 0	0 1··	·· 188	1 8·	1.11	0,·7	0,645	2 60	·· 48
·	20 7	1432 0	0 1·7	0 17·	1 77	1 42	0,5··	·830	3 ··	0 65
9	3· ·	2·8·0 0	0 16·	·0 1·7	1 43	1.18	0 ··	1 24	·	0 ·8
10	37 ·	2·~0 0	0.171	··,130	1 ·1	0,57	0	1,··	··	0,·8

Read·g 67 5 is proportional to v   0 310

TABLE 12
Table 29 of First Paper
Ī (C). 2.270 ; H₂SO₄ (D). 1.147 : H₃AsO₄ (E). 0.310 ; V. 0.155

No	Reading	t'	ı	E — ı	$K_1.10^4$	$K_1'.10^4$	$R.10$	$R_1.10^2$	$K_1''.10^4$	$K_1' \cdot 10^5$
1	0.0	0.0	0.00000	0.310	—				—	—
2	0.2	9.5	0.00092	0.309	—	—	—	—	—	—
3	1.2	70.0	0.00551	0.304	1.17	1.17	5.18	—	1.17	0.35
4	3.7	292.0	0.0175	0.293	0.819	0.817	5.51	0.21	0.848	0.28
5	13.1	991.0	0.0602	0.250	0.938	0.986	5.69	2.96	1.50	0.53
6	14.8	1175.0	0.0680	0.242	0.906	0.770	4.29	3.84	1.63	0.59
7	16.9	1430.0	0.0776	0.232	0.873	0.688	3.67	5.09	1.64	0.60
8	21.6	2470.0	0.0989	0.211	0.675	0.443	1.96	8.60	2.17	0.82
9	22.4	2880.0	0.102	0.208	0.590	0.20	0.95	0.2	2.17	0.82

Reading 67 is proportional to 0.310

TABLE 13
Ī (C), 2.27 . H₂SO₄ (D), 2.29 ; H₃AsO₄ (E). 0.1473 ; V. 0.1.

No.	Reading	t'	ı	E — ı	$K.10^4$	$K_1'.1$
1	0.0	0.0	0.0000	0.1473	—	—
2	0.3	1.25	0.0003	0.1470		—
3	3.25	16.8	0.0034	0.1438	0	6.06
4	10.85	95.5	0.01165	0.7	5.4	5.21
5	14.0	87.5	0.01503	0.13	5.	4.95
6	21.3	133.0	0.02287	0.124	5.4	5.82
7	27.5	182.	0.02953	0.178	5.1	4.88
8	7	225.5	0.03619	11	5.2	5.46
9	8	5	0.04959	10	5.39	5.83
				average	5.46	5.46

Reading 137.2 is proportional to 0.1473
Correction for direct rate negligible

TABLE 14

$\bar{I}$ (C), 2.27; H_2SO_4 (D), 2.29; H_3AsO_4 (E), 0.1473; V, 0.120; I_3 (A), 0.208

No.	Reading	θ	x	$E - x$	$K_1 \cdot 10_4$	$K_1' \cdot 10^4$
1	0.0	0.0	0.0000	0.1473	—	—
2	0.75	1.5	0.00081	0.1465	—	—
3	3.8	18.5	0.00408	0.1432	5.76	5.76
4	11.75	64.5	0.01262	0.1347	5.80	5.80
5	15.05	87.5	0.01615	0.1311	5.48	5.05
6	21.65	135.0	0.02325	0.1240	5.39	5.07
7	28.5	182.0	0.03061	0.1167	5.46	5.02
8	35.25	228.5	0.03785	0.1095	5.60	5.99
9	38.3	258.0	0.04113	0.1062	5.45	5.64

Average   5.56   5.47

Reading 137.2 is proportional to x 0.1473
Correction for direct rate is negligible

TABLE 15

$\bar{I}$ (C), 2.27; H_2SO_4 (D), 2.29; H_3AsO_4 (E), 0.1473; V, 0.120; H_3AsO_4 (B), 0.206

No	Reading	θ	x	$E - x$	$K_1 \cdot 10^4$	$K_1' \cdot 10^4$
1	0.0	0.0	0.0000	0.1473	—	—
2	0.4	1.75	0.00043	0.1469	—	—
3	3.1	17.0	0.00333	0.1440	5.48	5.48
4	10.6	59.0	0.01138	0.1359	5.91	5.95
5	14.7	87.5	0.01579	0.1315	5.58	5.02
6	20.8	133.5	0.02234	0.1250	5.32	6.07
7	27.4	181.0	0.02943	0.1179	5.30	5.35
8	33.25	227.0	0.03571	0.1116	5.26	5.18
9	36.9	257.0	0.03963	0.1077	5.27	5.20

Average   5.44   5.46

Reading 137.2 is proportional to x 0.1473
Correction for the direct rate is negligible

TABLE 16

Ï (C). 4.80; H_2SO_4 (D). 4.79; H_3AsO_4 (E). 0.437; V. 0.500

No.	Reading	t	r	E − 1	$K_1.10^4$	$K'.10^4$	$R.10^4$	$R_1.10^4$	$K_1''.10^4$	$K'.10^6$	$K_3'.10^{-5}$ / K_5'	$M.10^4$
1	0.0	0.0	0.0000	0.437	—	—	—	—	—	—	—	—
2	1.3	114.5	0.0116	0.4254	—	—	—	—	—	—	—	—
3	3.74	324	0.0332	0.4038	1.08	1.08	2.35	0.014	1.08	1.34	1.96	2.67
4	6.17	548	0.0548	0.3822	1.07	0.62	0.546	0.038	0.66	0.87	3.01	2.54
5	12.45	1256	0.1106	0.3264	1.01	0.468	0.678	0.155	1.19	1.55	1.70	2.74
6	14.42	1555	0.1281	0.3089	0.97	0.800	0.568	0.208	1.09	1.42	1.85	2.83
7	16.7	1950	0.1483	0.2887	0.91	0.744	0.494	0.278	1.16	1.51	1.74	2.49
8	19.9	2707	0.1768	0.2602	0.82	0.596	0.357	0.397	1.26	1.64	1.60	2.06
9	20.86	2951	0.1853	0.2517	0.81	0.590	0.342	0.434	1.34	1.75	1.50	1.88
10	21.69	3242	0.1927	0.2443	0.77	0.447	0.251	0.472	1.29	1.68	1.56	1.88
11	23.43	4190	0.2081	0.2289	0.66	0.299	0.157	0.548	1.50	1.96	1.34	1.53
12	23.9	4804	0.2123	0.2247	0.59	0.130	0.067	0.570	1.23	1.61	1.63	1.83
13	24.47	5622	0.2173	0.2197	0.52	0.119	0.060	0.597	1.30	1.70	1.54	1.69
14	24.55	6121	0.2180	0.2190	0.48	0.028	0.014	0.603	1.23	1.61	1.63	1.78
15	25.34	7060	0.2250	0.2120	0.44	0.150	0.073	0.642	1.47	1.92	1.37	1.44
16	25.66	7568	0.2279	0.2091	0.41	0.118	0.057	0.659	1.49	1.94	1.35	1.40
17	25.85	8502	0.2296	0.2074	0.37	0.038	0.018	0.670	1.44	1.88	1.39	1.44

Reading 19.2 is proportional to $x = 0.437$

Using the equilibrium formula gives

K_0 1.44 10⁵ from line 16

$K_6 = $ 1.40 10⁵ from line 17

Table 17

$\bar{T}_1$ (A), 0.438 : H_3AsO_3 (B), 0.439 ; $\bar{T}$ (C), 4.39 : H_2SO_4 (D), 4.37 : V, 0.500

No.	Reading	t		E — t	$K_1 \cdot 10^4$	$K_1' \cdot 10^4$	$R \cdot 10$	$R_1 \cdot 10^5$	$K_1'' \cdot 10^5$	$K_3' \cdot 10^6$	$\dfrac{K_3'}{K_2} \cdot 10^{-4}$
1	—	0.0									
2	3.13	1.5	0.0278	0.4092							
3	4.45	104.0	0.0395	0.3975	1.24	1.24	1.13	0.021	1.26	1.68	1.55
4	6.76	319	0.0600	0.3770	1.12	1.07	0.928	0.049	1.13	1.50	1.73
5	13.3	1027	0.1181	0.3189	1.05	1.03	0.754	0.188	1.29	1.72	1.51
6	15.5	1319	0.1377	0.2993	1.11	0.945	0.051	0.257	1.32	1.76	1.48
7	17.8	1721	0.1581	0.2789	0.96	0.754	0.484	0.337	1.28	1.70	1.53
8	21.1	2478	0.1874	0.2496	0.87	0.642	0.368	0.472	1.47	1.95	1.34
9	21.93	2722	0.1948	0.2422	0.84	0.537	0.299	0.513	1.46	1.94	1.35
10	22.65	3013	0.2011	0.2350	0.79	0.394	0.213	0.545	1.40	1.86	1.40
11	24.45	3963	0.2171	0.2198	0.68	0.323	0.163	0.635	1.58	2.10	1.24
12	25.1	4574	0.2229	0.2141	0.62	0.187	0.092	0.671	1.55	2.00	1.39
13	25.61	5369	0.2275	0.2095	0.54	0.115	0.0553	0.701	1.58	2.10	1.24
14	25.94	5902	0.2304	0.2066	0.50	0.122	0.0461	0.714	2.02	2.69	0.97

Reading 49.2 is proportional to t   0.438

Using the equilibrium formula gives

K_4 1.45 10^3 for line 13

K_5 1.36 10 for line 14

TABLE 18

$\bar{I}$ (C), 2.636; H_2SO_4 (D), 4.82; H_3AsO_4 (E), 0.2835; V, 0.120
Temperature 10° C

No.	Reading	θ	t	$\cdot E - x$	$K_1.10^3$
1	0.0	0.0	0.0000	0.2835	—
2	0.8	0.83	0.00314	0.2804	—
3	1.9	3.0	0.00746	0.2760	3.10
4	4.8	8.0	0.01885	0.2647	3.49
5	10.85	19.2	0.04260	0.2409	3.58
6	16.8	31.7	0.0660	0.2175	3.57
7	24.3	50.3	0.0954	0.1881	3.51
8	33.7	75.7	0.1323	0.1512	3.57
9	39.3	102.2	0.1543	0.1292	3.32

Average 4-8   3.54

Reading 72.2 is proportional to x 0.2835

TABLE 19

$\bar{I}$ (C), 2.636; H_2SO_4 (D), 9.64; H_3AsO_4 (E), 0.2835; V, 0.120
Temperature 10° C

No.	Reading	θ	x	$E - x$	$K_1.10^3$
1	0.0	0.0	0.00000	0.2835	—
2	2.25	1.0	0.00884	0.2747	—
3	15.6	8.25	0.06126	0.2222	12.7
4	19.8	11.0	0.07775	0.2058	12.5
5	22.85	13.2	0.08973	0.1938	12.4
6	30.15	19.0	0.1184	0.1651	12.3
7	36.7	26.2	0.1441	0.1394	11.7
8	42.1	31.7	0.1653	0.1182	11.9
9	46.2	37.5	0.1814	0.1021	11.8

Average 4 — 6   12.4

Reading 72.2 is proportional to x 0.2835

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TABLE 20

Table	C	D	E	V	$K_1 \cdot 10^2$	C factor	D factor	C index	D index	$K_3 \cdot 10^6$
1	1.358	28.92	0.2835	0.12	5.4		9.0		3.71	6.5
2	1.358	19.28	0.2835	0.12	1.2	2.2	1.17			1.8
3	2.716	19.28	0.2835	0.12	2.7		5.4		2.41	1.6
4	2.716	9.64	0.2835	0.12	0.51	3.1	1.63			0.77
5	5.43	9.64	0.2835	0.12	1.6		3.3		1.72	1.55
6	5.43	4.82	0.2835	0.12	0.49		2.9		1.54	0.70
7	5.43	2.41	0.2835	0.12	0.17	4.3		2.11		0.51
8	10.88	4.82	0.2835	0.12	2.1	4.4		2.14	1.48	1.51
9	10.88	2.41	0.2835	0.12	0.74		2.8		1.38	1.13
10	10.88	1.21	0.2835	0.12	0.27		2.6			0.84
11	2.270	2.293	0.310	0.155	0.024		2.0		1.0	0.39
12	2.270	1.147	0.310	0.155	0.012					0 38
13	2.27	2.29	0.1473	0.12	0.055					0.42
14	2.27	2.29	0.1473	0.12	0.056	(initial I_2)				
15	2.27	2.29	0.1473	0.12	0.055	(initial H_3AsO_4)				
16	4.80	4.79	0.437	0.500	0.011					1.34
17	4.83	4.82	0.439	0.500	0.013					1.68
18	2.636	4.82	0.2835	0.12	0.354	(Temperature 10°C)				
19	2.636	9.64	0.2835	0.12	1.24	(" ")				

Temperature coefficient (for 10° C)

Nos. 4 and 18 give 0.354   3.3 0.51   2.30

Nos. 4 and 19 give   1.24 0.51   2.44

TABLE 21

$\overline{I}$ (C), 4.80; H_2SO_4 (D), 4.79; H_3AsO_3 (E), 0.437; V, 0.500

No.	Reading	θ	A	r	r	$K_1.10^4$	$K_1'.10^4$	$R'.10^4$	$R_2.10^4$	$K_1''.10^5$
1	—	0.0		—	—				—	—
2	38.5		2.00	.3419	0.0951	—	—	—	—	—
3	37.1	117	0.3295	0.1075	9.56	9.56	1.04	0.368	1.30
4	35.0	321	0.3108	0.1262	9.19	8.97	0.868	0.432	1.35
5	33.5	549	0.2975	0.1395	7.97	6.27	0.564	0.478	1.15
6	29.7	1255	0.2638	0.1632	6.93	6.09	0.534	0.559	1.24
7	28.85	1556	0.2562	0.1808	6.32	3.72	0.238	0.619	1.37
8	27.87	1950	0.2475	0.1895	5.74	3.50	0.215	0.649	1.41
9	26.67	2708	0.2369	0.2001	4.80	2.37	0.133	0.685	1.46
10	26.57	2952	0.2360	0.2010	4.44	0.656	0.0365	0.690	1.30
11	26.38	3243	0.2343	0.2027	4.04	1.10	0.0602	0.695	1.38
12	26.14	4192	0.2320	0.2050	3.32	0.432	0.0233	0.702	1.34
13	25.78	4805	0.2290	0.2080	3.00	0.930	0.0488	0.713	1.45
14	25.61	5633	0.2274	0.2096	2.61	0.362	0.0187	0.718	1.43
15	25.80	6119	0.2291	0.2079	—				
16	25.82	7057	0.2293	0.2077	—			—	—

Average 1.35

Reading 49.2 is proportional to r 0.437
K_1'' 1.35 10^{-5} gives K_1' 0.262

TABLE 22

$\overline{I}$ (A), 0.438; H_3AsO_3 (B), 0.439; H_2SO_4 (D), .437; $\overline{I}$ (C) 4.39; V, 0.500

No.	Reading	θ	A	r	r	$K_1.10^4$	$K_1'.10^4$	$R'.10^4$	$R_2.10^4$	$K_1''.10^5$
1		0.0			—	—			—	—	—
2	46.71		2.00	.4148	0.0222		—			—
3	44.4	105.00	.3943	0.0427	12.2	12.2	1.89	0.152	1.32
4	40.91	333.00	.3633	0.0737	10.4	9.52	1.25	0.263	1.15
5	33.8	1010	0.3002	0.1368	8.86	8.17	0.735	0.488	1.36
6	32.06	1332	0.2847	0.1523	7.60	6.19	0.503	0.542	1.3
7	30.2	1735	0.2632	0.1688	7.63	5.36	0.385	0.602	1
8	28.27	2491	0.2510	0.1860	6.31	3.39	0.213	0.663	1
9	27.83	2736	0.2471	0.1899	5.99	2.57	0.157	0.677	1.37
10	27.54	3026	0.2446	0.1924	5.55	1.41	0.0844	0.686	1.29
11	26.86	3976	0.2386	0.1984	4.47	1.08	0.0615	0.707	1.35
12	26.45	4589	0.2349	0.2021	4.02	1.09	0.0601	0.720	1.42
13	26.28	5413	0.2334	0.2036	3.48	0.328	0.0179	0.726	1.37
14	26.23	5903	0.2329	0.2041	3.19	0.184	0.0100	0.728	1.36
15	26.29	6843	0.2355	0.2035	—			—	—
16	26.37	7347	0.2342	0.2028	—			—	—

Average 1.34

Reading 49.2 is proportional to r 0.438
K_1'' 1.34 10^{-5} gives K_2' 0.260

TABLE 23

No.	$A + r$	$B + r$	$C \; r$	$D - r$	$E - r$	r	V	$K_n \cdot 10^{-s}$
1	0.0062	0.0062	0.310	0.602	0.130	0.0062	0.12	1.76
2	0.0916	0.0916	1.49	0.516	0.248	0.0916	0.12	1.26
3	0.269	0.269	2.895	0.97	0.077	0.296	0.12	1.18
4	0.258	0.258	2.057	2.27	0.0278	0.2577	0.12	0.91
5	0.081	0.079	1.044	0.648	0.334	—0.168	0.12	1.08
6	0.044	0.042	0.606	0.688	0.341	—0.205	0.12	0.94
7	0.084	0.081	0.909	0.522	0.539	—0.539	0.12	0.77
8	0.162	0.159	1.74	0.568	0.223	—0.0875	0.12	0.71
9	0.0134	0.425	1.00	0.86	0.0904	—0.0904	0.12	0.57
10	0.075	0.070	0.918	0.531	0.548	—0.548	0.12	1.08
11	0.072	0.070	1.053	0.657	0.313	—0.177	0.12	1.52

Nos. 10 and 11 Temperature $10° C$

Temperature coefficient (for $10° C$)

Nos. 7 and 10 give 1.41

Nos. 5 and 11 give 1.41

From rate temperature coefficients, 3.39 2.37   1.43

From coefficient for $20° C$ (of First Paper) 1.34

TABLE 24

I_1 (A). 0.519; H_3AsO_4 (B), 5.15; I (C), 4.54; H (D), 3.88; V, 0.600

No.	Reading	H	$A - a$	$K_1 \cdot 10^3$	$K_1 \cdot 10^2$
1	28.8	0.0	0.519	—	—
2	27.0	5.83	0.4865	—	—
3	26.2	12.0	0.4721	2.10	1.73
4	21.3	52.5	0.3838	2.20	2.15
5	19.25	76.0	0.3469	2.10	2.07
6	16.2	113.5	0.2919	2.06	2.07
7	13.45	154.5	0.2424	2.03	2.08
8	10.7	212	0.1928	1.95	2.04
9	8.65	271	0.1558	1.87	1.99
10	7.05	330	0.1270	1.80	1.91

Average 4–8   2.08

TABLE 25

$\bar{I}_3$ (A), 0.519; H_3AsO_4 (B), 5.15; $\bar{I}$ (C), 6.39; H (D), 3.88; V, 0.600

No.	Reading	θ	$A - x$	$K_1.10^3$	$K_1.10^2$
1	28.8	0.0	0.519	—	—
2	28.3	1.08	0.5100	—	—
3	27.9	6.33	0.5027	1.20	2.34
4	26.1	31.3	0.4705	1.16	2.15
5	24.3	56.5	0.4381	1.19	2.22
6	22.8	86.0	0.4108	1.10	2.08
7	20.9	118.0	0.3766	1.13	2.20
8	19.35	154.0	0.3487	1.08	2.07
9	17.25	201.0	0.3108	1.08	2.08
10	15.3	260	0.2757	1.03	2.02
11	14.05	303	0.2531	1.01	2.01
				Average 4–11	2.10

TABLE 26

$\bar{I}_3$ (A), 0.519; H_3AsO_4 (B), 5.15; $\bar{I}$ (C), 3.25; H (D), 1.94; V, 0.600

No	Reading	θ	$A - x$	$K_1.10^1$	$K_1.10^2$
1	28.8	0.0	0.519	—	
2	26.9	1.33	0.4847	—	—
3	25.8	3.50	0.4649	8.34	4.21
4	23.0	10.33	0.4145	7.55	3.79
5	19.25	18.8	0.3469	8.29	4.23
6	16.4	30.3	0.2955	7.42	3.92
7	12.3	46.0	0.2216	7.58	4.16
8	8.0	76.0	0.1441	7.20	4.08
9	6.62	92.0	0.1192	6.73	3.90
				Average 3–9	4.04

TABLE 27

I_1 (A), 0.519; H_3ASO_3 (B), 2.58; I (C), 4.55; H (D), 3.84; V, 0.600

No.	Reading	θ	A — x	$K_1 \cdot 10^3$	$K_1 \cdot 10^2$
1	28.8	0.0	0.519	—	—
2	28.6	1.33	0.5153	—	—
3	28.05	6.75	0.5055	1.55	2.96
4	26.8	22.8	0.4829	1.32	2.47
5	25.4	42.5	0.4577	1.25	2.41
6	23.45	75.5	0.4225	1.16	2.24
7	21.4	115.0	0.3856	1.11	2.16
8	19.05	161	0.3433	1.10	2.22
9	16.65	229	0.3000	1.03	2.10
10	15.24	272	0.2746	1.01	2.07
11	13.6	335	0.2450	0.97	2.04
				Average 5–10	2.20

TABLE 28

I_1 (A), 0.519; $H_3A sO_4$ (B), 5.15; I (C), 6.34; H (D), 3.88; V, 0.600
Temperature 10° C

No.	Reading	θ	A — x	$K_1 \cdot 10^3$	$K_1 \cdot 10^2$
1	26.8	0.0	0.519	—	—
2	26.6	1.5	0.5151	.	—
3	26.4	3.0	0.5113	2.27	4.16
4	24.95	9.0	0.4832	3.72	6.70
5	22.75	20.5	0.4406	3.55	6.45
6	19.65	38.2	0.3805	3.57	6.78
7	16.1	64.2	0.3118	3.48	6.61
8	14.15	83.2	0.2740	3.36	6.53
9	10.72	130.0	0.2076	3.08	6.10
				Average 4–8	6.61

TABLE 29

I_1 (A), 0.519; H_3AsO_4 (B), 5.15; $\bar{I}$ (C), 4.57; H (D), 1.94; V, 0.600
Temperature 10° C

No.	Reading	θ	A — x	K_1 10^3	K_1 10^3
1	26.4	0.0	0.519	—	—
2	24.55	1.5	0.4826	—	—
3	23.35	3.67	0.4571	10.8	10.4
4	19.5	8.5	0.3834	14.3	14.1
5	16.5	14.3	0.3243	13.5	13.6
6	14.4	19.5	0.2831	13.0	13.2
7	12.5	24.5	0.2457	12.7	13.2
8	10.6	31.0	0.2084	12.4	13.0
9	9.45	35.5	0.1857	12.2	13.1
10	7.78	43.5	0.1530	11.9	12.9

Average 4–10   13.3

TABLE 30

Table	A	B	C	D	K_1 10^3	K_1 10^3	K_1	Temp.
24	0.519	5.15	4.53	3.88	2.11	2.08	0.135	0°
25	0.519	5.15	6.39	3.85	1.13	2.10	0.136	0°
26	0.519	5.15	3.25	1.94	8.3	4.04	0.131	0°
27	0.519	2.58	4.55	3.84	1.11	2.20	0.139	0°
						Average	0.135	
28	0.519	5.15	6.34	3.88	3.5	6.61	0.427	10°
29	0.519	5.15	4.57	1.94	14.0	13.3	0.430	10°
						Average	0.428	

Temperature coefficient (for 10° C.) 0.428 0.135   3.17

TABLE 31

I (C) 6.54; H (D) 4.91; H_3AsO_4 (E) 0.2835; V, 0.120

No.	Reading	θ	x	E — x	K_1 10^3
1	0.0	0.0	0.0000	0.2835	—
2	2.95	1.0	0.01065	0.2728	—
3	8.8	3.75	0.03173	0.2518	1.27
4	19.35	9.25	0.0698	0.2137	1.3?
5	29.6	16.0	0.1068	0.1767	1.28
6	39.6	23.5	0.1406	0.1429	1.26
7	43.8	30.0	0.1580	0.1255	1.17
8	52.6	38.8	0.1897	0.0938	1.25
9	57.4	47.0	0.2070	0.0765	1.21
10	62.0	57.0	0.2236	0.0599	1.18

Reading 78.6 is proportional to x 0.2835

TABLE 32

$\overline{I}$ (C), 3.27; II (D), 4.91; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	t	E − v	$K_1 \cdot 10^5$
1	0.0	0.0	0.0000	0.2835	—
2	1.8	1.0	0.00649	0.2770	—
3	5.45	6.5	0.01965	0.2638	3.85
4	13.3	17.5	0.04797	0.2355	4.27
5	19.2	27.3	0.06925	0.2142	4.26
6	24.95	37.5	0.0900	0.1935	4.28
7	29.4	46.8	0.1060	0.1775	4.19
8	36.0	61.8	0.1298	0.1537	4.19
9	40.2	72.5	0.1450	0.1385	4.19
10	45.0	88.3	0.1623	0.1212	4.10
11	51.6	115.0	0.1861	0.0974	3.99

Reading 78.6 is proportional to v   0.2835

TABLE 33

$\overline{I}$ (C), 3.27; II (D), 2.46; H_3AsO_4 (E), 0.2835; V, 0.120

No.	Reading	θ	t	E − v	$K_1 \cdot 10^5$
1	0.0	0.0	0.0000	0.2835	
2	0.05	1.25	0.00018	0.2833	—
3	1.35	6.25	0.00487	0.2786	1.48
4	5.05	24.3	0.01821	0.2653	1.43
5	9.5	40.8	0.03426	0.2492	1.41
6	15.2	70.3	0.05485	0.2283	1.35
7	19.75	92.8	0.06743	0.2141	1.34
8	23.25	115.5	0.08386	0.1996	1.34
9	26.0	132.5	0.09378	0.1897	1.33
10	29.2	154.0	0.1053	0.1782	1.32

Reading 78.6 is proportional to v   0.2835

TABLE 34

I (C), 1.645; H (D), 2.46; H$_3$AsO$_4$ (E), 0.2835; V, 0.120

No.	Reading	θ	x	E — x	K$_1$.10^4
1	0.0	0.0	0.00000	0.2835	
2	0.0	1.0	0.00000	0.2835	—
3	0.4	4.33	0.00216	0.2813	5.73
4	3.2	43.0	0.01728	0.2662	6.28
5	5.55	77.3	0.02997	0.2536	6.23
6	8.7	126.0	0.04697	0.2365	6.23
7	13.5	207.0	0.07830	0.2052	6.75
8	18.25	310.0	0.09856	0.1849	5.96
9	23.0	35.0	0.1242	0.1593	5.76
				Average 4-8	6.29

Reading 52.5 is proportional to x 0.2835

TABLE 35

I (C), 3.27; H (D), 1.23; H$_3$AsO$_4$ (E), 0.2835; V, 0.120

No.	Reading	θ	x	E — x	K$_1$.10^4	K$_2$.10^2
1	0.0	0.0	0.00000	0.2835	—	—
2	0.0	1.25	0.00000	0.2835	—	—
3	1.3	15.0	0.00702	0.2765	7.23	7.12
4	3.65	52.5	0.01971	0.2638	5.60	6.02
5	6.8	113.0	0.03672	0.2468	5.30	5.57
6	10.75	195.0	0.05805	0.2254	5.12	5.19
7	15.35	297.0	0.0829	0.2006	5.10	5.21
				Average 4-7		5.45

Reading 52.5 is proportional to x 0.2835

TABLE 36

I (C), 3 27; H (D), 4.91; H_3AsO_4 (E), 0.2835; V, 0.120
Temperature 10° C

No	Reading	θ	t	$E - x$	K_1 10^3
1	0.0	0.0	0.00000	0.2835	—
2	2.05	1.0	0.00805	0.2755	—
3	7.35	4.0	0.02886	0.2546	11.4
4	12.25	7.25	0.04810	0.2354	11.9
5	16.05	10.5	0.06656	0.2169	10.8
6	22.2	14.7	0.08718	0.1963	10.8
7	26.8	18.8	0.1052	0.1783	10.7
8	33.9	25.8	0.1331	0.1504	10.6
9	40.8	34.7	0.1602	0.1233	10.4
10	48.4	47.5	0.1900	0 0935	10.1

Average 4–8   10.7

Reading 72.2 is proportional to x 0.2835

TABLE 37

Table	C	D	E	V	K_1 10^2	C factor	D factor	K 10^6
31	6.54	4.95	0.2835	0.12	1.33			1.05
						3.1		
32	3.27	4.95	0.2835	0.12	0.427			1.06
							3.0	
33	3.27	2.45	0.2835	0 12	0.143	2.3		0.71
34	1.645	2 46	0.2835	0.12	0.062		2 5	0 64
35	3.27	1.23	0.2835	0.12	0.056			0.55
36	3.27	4.96	0.2835	0.12	1.07			

Table 36. Temperature 10° C
Temperature coefficient (for 10° C)
Nos 32 and 36 give 2 51

TABLE 38

No	A	B	C	D	E		N	K b
1	0.102	0.101	1.372	0.584	0.173	.101	0.12	0.786
2	0.0062	0.0055	0.64	0.00	0.2	0.547	.1	0.822
3	0.667	0.667	3.00	4.83	0.015	.667	.12	1.03
4	0.114	0.500	1.74	1.54	0.122	.146	0.12	0.76
5	0.038	0.036	0.715	0.42	1	.1	0.12	0.613
6	0.133	0.131	2.05	0.380	2.3	.1	0.12	0.871
7	0.265	0.250	1.5	52	0.185	.152	0.12	0.527
8	0.050	0.04	3	0.08		0.149	0.12	0.503
9	0.268	0.518	1.74			0.08	0.12	0.382
10	0.382	0.380	2.73	3	0.0	1.33	0.12	0.364
11	0.500	0.503	1.74	1.34	0.08	0.0093	0.12	1.09
12	0.034	0.032	0.710	0.479	0.2	0.215	.12	0.8
13	0.248	0.242	1.28	0.89	0.100	0.409	.12	0.68
14	0.046	0.44	0.707	0.467	.40	0.203	0.12	0.624

Nos. 11, 12, 13, 14 temperature 0 C

Temperature coefficient for 1 C

Nos. 4 and 11 give 1.4

" 5 and 12 give 1.33

" 7 and 13 give

" 8 and 14 give

Average 1.25

From the rate temperature coefficients 3.17 2.51 1.27