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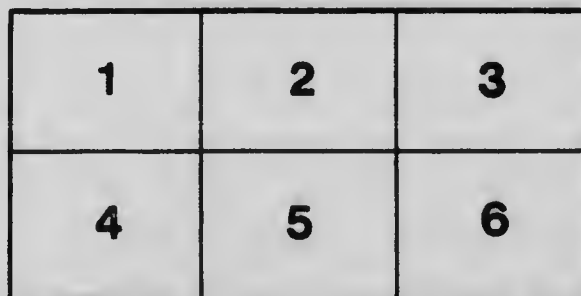
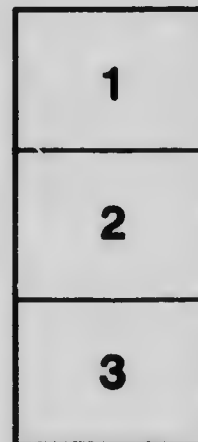
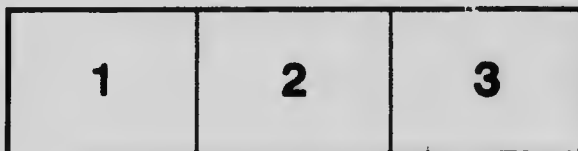
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PAPERS
FROM THE
CHEMICAL LABORATORY.

No. 28.—The Rate of Oxidation of Potassium
Iodide by Chromic Acid.

BY

RALPH E. DELURY.

Reprinted from the Journal of Physical Chemistry,
Vol. VII, April, 1903.

TORONTO, 1903.



"With the exception of
of the results"

**THE RATE OF OXIDATION OF POTASSIUM
IODIDE BY CHROMIC ACID**

By RALPH E. DeLURY

Reprinted from the Journal of Physical Chemistry, Vol 7, No. 1, April, p. 237, 1903



THE RATE OF OXIDATION OF POTASSIUM IODIDE BY CHROMIC ACID

BY RALPH E. DELURY

The present measurements, like those of the rate of oxidation of ferrous salts¹ by chromic acid, were undertaken with a view of throwing light on the remarkable catalytic action of iron on the oxidation of iodides; and also in order to ascertain whether the irregularities observed in the oxidation of ferrous sulphate² and of sodium thiosulphate³ were inherent to the use of chromic acid as an oxidizing agent.

With the exception of Series VI the measurements were carried out at 30° C. Two of the reagents, suitably diluted, were mixed in a wide mouthed Erlenmeyer flask of 200 or 300 cc capacity while the third (usually the substance present in least quantity) was pipetted into a test tube, together with enough water to make up 15 cc. Both vessels were left in the thermostat until the proper temperature was attained, when the test-tube was taken out, quickly covered with a cloth to hinder loss of heat, and at the right moment emptied into the flask. The mixture was shaken and the last drops of liquid were removed from the tube by tapping it against the walls of the Erlenmeyer.

When it was desired to stop the reaction, a "restrainer" was poured in, consisting of a solution of sodium acetate in which was dissolved sufficient sodium bicarbonate to neutralize somewhat less than nine-tenths of the sulphuric acid initially present in the reacting mixture. The iodine liberated was then determined with $n/100$ sodium thiosulphate and iodine solutions, using starch⁴ as indicator; a sharp end point was ensured by

¹ Jour. Phys. Chem. 7, 1 (1903).

² Ibid. 7, 10 (1903).

³ Ibid. 7, 81 (1903).

⁴ If a few crystals of menthol be left floating on the starch solution, it keeps good for weeks; the solution of sodium acetate was preserved from decomposition by the same means.

adding about one cubic centimeter of a normal solution of potassium iodide before titrating.

The efficiency of the restrainer was tested by letting the mixture stand half an hour or so after titration; no blue colour, indicating liberation of iodine, was observable.

Blank experiments showed that (probably owing to the short duration of the experiments) there was no necessity for special precautions to exclude air or to prevent loss of iodine by evaporation; the mouth of the Erlenmeyer flask was simply closed by a watch glass.

The stock solutions were:—*Potassium bichromate*, $F/10^1$ (0.6 normal), made up by weighing the pure salt. *Potassium iodide*, approximately $F/10$, standardized gravimetrically with silver. *Sulphuric acid*, approximately $F/2$, standardized gravimetrically with barium. The alkalinity of the iodide solution was determined, and has been allowed for in giving the initial compositions of the reacting mixtures.

The volumetric solutions of iodine and thiosulphate were frequently compared with a solution of sodium arsenite whose titer was determined against freshly sublimed iodine.

All pipettes used were calibrated by weighing the distilled water delivered, an interval of thirty seconds being allowed for drainage.

Classification of the Measurements

The experiments may be grouped in six Series.

In *Series I*, the concentration of the bichromate was much less than those of the other reagents. Expts. 1-6.

In *Series II* the concentration of the iodide was much less than those of the other reagents. Expts. 7-11.

In *Series III* bichromate and iodide were present in comparable amounts, the acid in excess. Expts. 12-14.

Series IV includes experiments on the influence of each of the three reagents, by the Method of Constant Rates; Expts. 15-17.

¹ One formula weight in ten liters.

Series V contains experiments on the catalytic action of a number of salts; Table 18. Finally the experiments of *Series VI* were carried out at 0°C, to determine the influence of the temperature on the rate; Expts. 19-27.

Explanation of the Tables

At the head of each table the total volume of the reacting mixture is given, and the quantities of the reagents initially present, in the following units. The letter *A* denotes the number of gramme-formula-weights of potassium bichromate ($K_2Cr_2O_7$) multiplied by 100,000; *B*, the number of gramme-formula-weights of sulphuric acid (H_2SO_4) multiplied by 100,000; and *C* the number of gramme-formula-weights of potassium iodide, (KI) also multiplied by 100,000. *V* is the volume in cubic centimeters. Under *x* is entered the amount of iodine liberated in θ minutes, expressed in cubic centimeters of $n/100$ thiosulphate. The amount of iodine dissolved in the potassium iodide of experiments *i-iii*, Table 18, is expressed in the same units.

The value of *x* for $\theta = \infty$ (that is, the number of cubic centimeters of $n/100$ thiosulphate equivalent to the iodine that would be liberated if the reaction were allowed to proceed until none of the reagent present in least quantity remained) was obtained by calculation from the known initial composition of the reacting mixture; in the measurements of Series I this value was controlled by direct experiment; in Series II a similar check was not feasible.

RESULTS OF THE MEASUREMENTS

Series I

The first Series were carried out with potassium bichromate in small quantity, as it was thought that the iodine liberated by the reaction might exert less influence on the rate in presence of a large excess of potassium iodide, than if the quantity of the latter were small. Experiments *i* and *ii*, Table 18, show that the retardation due to this cause would not seriously affect the results of the measurements.

The constancy of k_1 throughout each of the tables, and the fact that doubling the concentration of the bichromate does not affect that constant (Expts. 1 and 2; 3 and 4) shows that the rate is proportional to the concentration of the bichromate. Doubling the concentration of the iodide trebles the rate (Expts. 5 and 2), and doubling that of the acid quadruples it. Thus, the rate is proportional to the concentration of the bichromate, and to the square of that of the acid.

EXPTS. 1 AND 2.

1. A , 1.968; B , 237.9; C , 142.4; V , 100; k_{avg} , 0.0065; R , 0.18
 2. A , 0.984; B , 237.9; C , 142.4; V , 100; k_{avg} , 0.0066; R , 0.088

1. θ	x	k_1	2. θ	x	k_1
5	0.75	(0.0057)	10	0.75	(0.0059)
10	1.60	0.0063	15	1.21	0.0067
15	2.43	0.0067	20	1.50	0.0064
20	3.00	0.0064	25	1.90	0.0067
30	4.31	0.0066	30	2.18	0.0067
∞	11.81	—	∞	5.90	—

EXPTS. 3 AND 4.

3. A , 1.968; B , 478.3; C , 142.4; V , 100; k_{avg} , 0.029; R , 0.792
 4. A , 0.984; B , 478.3; C , 142.4; V , 100; k_{avg} , 0.029; R , 0.396

3. θ	x	k_1	4. θ	x	k_1
2.5	1.68	0.0307	2.5	0.82	0.0260
5.0	3.21	0.0276	5.0	1.78	0.0312
7.5	4.57	0.0283	7.5	2.42	0.0306
10.0	5.78	0.0292	10.0	2.87	0.0289
15.0	7.60	0.0299	15.0	3.71	0.0287
∞	11.81	—	∞	5.90	—

EXPTS. 5 AND 6.

5. A , 0.984; B , 235.3; C , 284.9; V , 100; k_{avg} , 0.019; R , 0.260
 6. A , 0.984; B , 117.7; C , 142.4; V , 100; k_{avg} , 0.002; R , 0.026

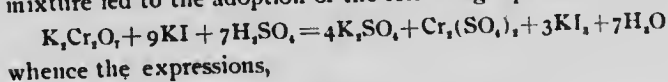
5. θ	x	k_1	6. θ	x	k_1
5	1.18	0.0194	10	0.24	0.00180
10	2.16	0.0197	20	0.48	0.00184
15	2.74	0.0181	40	1.01	0.00204
20	3.46	0.0192	—	—	—
∞	5.90	—	∞	5.90	—

$$^1 k_1 = 1/\theta \cdot \log_{10} 6A/(6A - x).$$

At the head of each Table of this Series, I have noted the average value of k_1 (omitting those enclosed in brackets). Strictly speaking, k_1 should diminish as the reaction proceeds; owing to the large excess of iodide and acid however, the diminution could never exceed a few percent, and is of the same order as the experimental errors. R is calculated from the average value of k_1 by the relation $R = dx/d\theta = 6k_1A \times \log_{\text{nat}} 10$.

Series II

In Series II the amount of the potassium iodide in the reacting mixture was much less than that of the bichromate or that of the acid. A few experiments in which iodine was dissolved in the potassium iodide before making up the reacting mixture led to the adoption of the following equation,



$$6A - x, \quad 6/7B - x, \quad 2/3C - x,$$

to represent the amounts of bichromate, acid and iodide remaining when the iodine liberated was equivalent to $x \times 10^{-3}$ gramme-formula-weights of sodium thiosulphate.

The details of the measurements in question are not published in the present paper; it is hoped that the results of an investigation of the reaction between iodic and hydriodic acids which has been undertaken in this laboratory, may throw light on the retardation caused by iodine.

EXPTS. 7 AND 8.

7. $A, 19.9; B, 240.3; C, 9.45; V, 100; K_{\text{avg}}, 26 \times 10^{-10}; R, 0.083$
 8. $A, 19.9; B, 480.7; C, 9.45; V, 100.$

7. θ	x	$K \times 10^{10}$	8. θ	x	$T(\theta)$	T/θ	$K \times 10^{10}$
5	0.39	26	5	1.47	20	4	26
10	0.78	26	10	2.69	44	4.4	28
15	1.13	26	15	3.85	80	5	32
20	1.45	26	20	4.66	—	—	34
30	1.93	24	25	5.37	—	—	40
40	2.54	26	30	5.80	—	—	44
60	3.32	26					
80	3.84	24					

EXPTS. 9 AND 10.

9. $A, 39.8; B, 240.3; C, 9.45; V, 100; K_{avg}, 22 \times 10^{-10}; R, 0.141$
 10. $A, 39.8; B, 240.0; C, 18.89; V, 100; K_{avg}, 20 \times 10^{-10}; R, 0.257$

9. θ	x	$T(7)$	T/θ	$K \times 10^{10}$	10. θ	x	$T(9)$	T/θ	$K \times 10^{10}$
5	0.52	—	—	(18)	5	1.26	11	2.2	21
10	1.10	15	1.5	20	10	2.47	24	2.4	22
15	1.75	27	1.8	22	15	3.20	32	2.0	20
20	2.25	35	1.8	23	20	3.71	39	2.0	18
25	2.53	40	1.6	21	26	4.64	55	2.0	18
30	3.06	57	1.9	23	30	5.56			20
40	3.77	77	1.9	24					
50	4.32	—	—	(24)					

EXPT. 11.

$A, 39.8; B, 480.7; C, 9.45; V, 100; K_{avg}, 27 \times 10^{-10}; R, 0.694$

θ	x	$T(8)$	$T(8)/\theta$	$T(9)$	$T(9)/\theta$	$K \times 10^{10}$
2.5	1.31	4.5	1.8	12	5	24
5.0	2.64	10	2.0	26	5	27
10.0	4.11	18	1.8	46	4.6	27
15.0	5.15					29

Comparing Expts. 7 and 9, it is apparent that halving the concentration of the bichromate approximately doubles the time necessary for the liberation of a given quantity of iodine; $T(7)$ in Table 9 (obtained from Expt. 7 by interpolation) being the time required to free x units when $A = 19.9$, and θ the time when $A = 39.8$ (compare also Expts. 8 and 11).

Similarly, doubling the concentration of the iodide doubles the rate (Expts. 7 and 10), while doubling that of the acid somewhat more than quadruples it (Expts. 8 and 7; 11 and 9).

The values of K in Tables 7 to 11 are calculated from the integrated form of the equation

$$R = dx/d\theta = K(6A - x)(6/7B - x)(2/3C - x) \dots (1)$$

Except in the case of Table 8 the values are fairly constant, affording further evidence that in first approximation at all events, the rate is proportional to the concentrations of the bichromate and of the iodide, and to the square of that of the acid.

With respect to the bichromate and the acid, therefore, the

general results of these measurements confirm those of Series I. In the case of the iodide, however, the effect of doubling the concentration differs in the two Series.

The experiments of

Series III

in which the concentrations of the reagents in question were intermediate between their values in Series I and those in Series II, were undertaken in order to obtain further light on this matter.

As the concentration of the acid remained practically unaltered during the progress of the reaction, it was allowable to treat $(6/7B - x)$ as constant during the integration of Equation (1), thus obtaining

$$k_2 = 36KB^2/49 = 1/0(c-a) \cdot \log \text{nat} (c-x)a/(a-x)c$$

(a being written for $6A$, and c for $2/3C$).

EXPTS. 12, 13 AND 14.

12. $A, 7.91; B, 239.4; C, 56.97; V, 100; k_2, \text{avg}, 13 \times 10^{-5}; R, 0.23$
 13. $A, 7.91; B, 240.1; C, 18.89; V, 100; k_2, \text{avg}, 11 \times 10^{-5}; R, 0.068$
 14. $A, 2.637; B, 239.4; C, 56.97; V, 100; k_2, \text{avg}, 13 \times 10^{-5}; R, 0.077$

12. θ	x	$k_2 \times 10^5$	13. θ	x	$k_2 \times 10^5$	14. θ	x	$k_2 \times 10^5$
5	1.11	13	5	0.22	(7)	10	0.71	12
10	2.24	13	15	0.96	11	15	1.10	13
15	3.24	13	20	1.23	11	20	1.50	13
20	4.26	13	30	1.84	11	30	2.12	13

Reference to the Tables containing the results of Expts. 12, 13 and 14 shows that trebling the concentration of the bichromate leaves k_2 unaltered, i. e. trebles the rate, while trebling that of the iodide increases k_2 , i. e. more than trebles the rate.

Deviation from strict proportionality between rate and concentration, therefore, occurs in the case of the iodide, and not noticeably in the case of the bichromate.

Series IV

In order to study this deviation more thoroughly, free from the restriction that one or other of the reagents must be present in relatively small quantity, the measurements of this Series

were carried out by the "Method of Constant Rates" described in a recent paper by Bray.¹

The restrainer being added, and the solution analyzed before the concentrations of the reagents had been much reduced by the progress of the reaction, the quotient x/θ gives a first approximation to the rate; the effect due to the slight decrease in the concentrations (12 percent at most), was corrected by means of equation 1.

EXPT. 15.

$A, 17.79; C, 94.83 \times n; V, 200.$

B	n	θ	x	R	$R \text{ corr.}$	$R \text{ calc.}$
239.6	0.5	80	3.01	0.040	0.040	0.045
238.7	1	80	7.52	0.11	0.11	0.10
237.0	2	36	8.08	0.23	0.24	0.24
235.3	3	35	13.01	0.38	0.40	0.42
233.6	4	17	9.76	0.64	0.68	0.64
231.9	5	10	8.05	0.88	0.94	0.90
230.2	6	11	11.31	1.17	1.28	1.20
228.5	7	9	11.30	1.42	1.57	1.54
226.8	8	8	12.47	1.78	2.01	1.92
225.1	9	6	11.55	2.19	2.49	2.34
223.4	10	5	11.00	2.47	2.86	2.80

EXPT. 16.

$A, 17.79; C, 94.83; V, 200.$

B	θ	x	R	$R/B^2 \times 10^6$
118.5	80	2.96	0.039	2.80
238.7	80	7.52	0.11	1.87
479.2	20	7.66	0.42	1.85
729.6	10	8.59	0.95	1.80
960.0	5	8.30	1.83	1.99
1200.4	3	8.25	3.02	2.10

The results of these measurements are given in Tables 15, 16, and 17, and graphically in Fig. 1. Owing to the alkalinity of the stock solution of potassium iodide, the concentration of the acid varied from case to case in Expt. 15; under "R corr"

¹ Jour. Phys. Chem. 7, 93 (1903).

is given the rate calculated for $B = 240.4$, on the assumption that R is proportional to B^n . The corrected values of R are plotted in the figure.

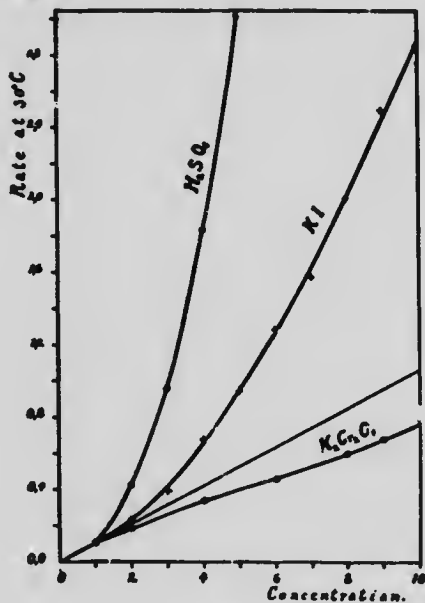


Fig. 1

EXPT. 17.

$A, 17.79 \times n$; $B, 238.7$; $C, 94.83$; $V, 200$.

n	θ	x	R	R/n
0.5	80	4.43	0.06	0.12
1	80	7.52	0.11	0.11
2	40	6.70	0.18	0.09
4	20	6.26	0.34	0.08
6	15	6.22	0.45	0.08
8	10	5.85	0.59	0.07
9	10	6.24	0.67	0.07
10	8	5.82	0.77	0.08

If the rate were strictly proportional to the concentrations

of the bichromate and of the iodide, the values of R from Expts. 15 and 17 should all lie on the straight line drawn through the first two measurements in Fig. 1. As may be seen by a glance at the figure, the rate is somewhat less than proportional to the concentration of the bichromate, and much more than proportional to that of the iodide. It is very closely proportional to the square of the concentration of the acid (see the quotient R/B^2 in Table 16).

The deviation in the case of the bichromate may be ascribed to decrease in the dissociation of the chromic acid attendant on increase in its concentration, the rate being supposed proportional to the concentration of the ion Cr_2O_7 . It is only necessary to assume that in Expt. 17 ($n = 1$) ten percent of the chromic acid is undissociated, in order to account for the difference between the observed values and those of the straight line in Fig. 1.

That the potassium ions added with the bichromate are not responsible for the retardation is evidenced by Expt. vi, Table 18, in which potassium nitrate was present. In the absence of bichromate, no iodine was liberated; thus the possibility that retardation by the potassium was offset by action of the nitric acid, is excluded.

In the case of the iodide, the rates are reproduced with considerable accuracy by the formula

$$R_{\text{calc}} (\text{Expt. 15}) = 0.08n + 0.02n^2.$$

An explanation, in conformity with the prevalent theories connecting rate and mechanism of a reaction, and not in itself improbable, is afforded by the supposition that there are two different primary products of oxidation, one involving but one molecule of potassium iodide, and the other two molecules of that substance.

Bray's¹ experiments on the oxidation of potassium iodide by chloric acid (see his series J, also the foot note on page 108 of his paper), show that with this oxidizing agent as well as with chromic acid the rate increases more rapidly than the concen-

¹ Jour. Phys. Chem. 7, 92 (1903).

tration of the iodide; but the explanation suggested in the preceding paragraph, though plausible, cannot be considered well founded until the effect of dissolving iodine in the iodide has been thoroughly studied and satisfactorily accounted for. It is hoped that the experiments with iodic acid, already referred to, may prove of service in this connection.

Series V

Under this heading are collected the experiments in which the products of the reaction, and a number of salts which often exert an accelerating effect on the process of oxidation, were added to the reacting mixture.

TABLE 18.

No.	Catalyser	A	B	C	D	V	θ	x (Cal.)	x
i	Iodine	9.84	233	142.	10.65	100	5	+ 35	4.50
ii	"	19.9	240	9.45	7.97	100	20	1.00	1.45
iii	"	17.79	232	474.	7.56	200	10	8.11	8.05
iv	$\text{Fe}_2(\text{SO}_4)_3$	4.92	233	142.	12.5	100	10	27.5	4.65
v	"	29.8	240	9.45	12.5	100	15	2.35	1.86
vi	KNO_3	17.79	234	379.	20.	200	15	9.18	9.17
vii	K_2SO_4	17.79	232	474.	5.	200	10	8.10	8.19
viii	$\text{Cr}_2(\text{SO}_4)_3$	17.79	223	948.	1.7	200	4	9.70	9.15
ix	"	17.79	229	664.	1.7	200	7	9.60	9.31
x	"	124.5	239	94.8	1.7	200	13	7.18	7.34
xi	$\text{UO}_2(\text{NO}_3)_2$	1.968	239	94.8	1.0	100	16	2.61	2.48
xii	$\text{Co}(\text{NO}_3)_2$	1.968	239	94.8	1.0	100	15	2.51	2.47
xiii	MnCl_2	1.968	239	94.8	1.0	100	15	2.56	2.51
xiv	$\text{MO}_3(\text{NH}_4)_2$	1.968	239	94.8	1.0	100	15	2.52	2.42
xv	Na_2WO_4	1.968	239	94.8	1.0	100	15	2.42	2.42

y , (iv) 4.85; (v) 0.06; (vi) 0.00.

In Table 18 the amounts of bichromate, acid, and iodide, are entered in the columns headed *A*, *B*, and *C* respectively; the total volume in cubic centimeters, under *V*. The quantity of salt, etc. added is given under *D* in 10^{-3} gram-formula weights. The iodine liberated in θ minutes is given under " x (cat)", while under x is entered the result of blank experiments in the absence of the catalyser. Finally, in a few cases, the amount of iodine set free by the catalytic agent in the absence of bichromate, has been recorded at the foot of the table, after y .

Very few of the substances experimented with had any appreciable effect on the rate. The acceleration due to the chrome alum is somewhat greater than would be caused by the acid liberated by complete hydrolysis; and in the case of the ferric salt, the acceleration is too great to be ascribed to the ferrous sulphate formed by reduction, although increase in the concentration of the iodide, which increases the amount of ferrous salt formed, also greatly increases the acceleration.

Series VI

In order to find the temperature-coefficient of the reaction, I repeated Experiment 1 at zero. The surprisingly small effect on the rate caused by a drop of thirty degrees suggested the possibility that the nature of the reaction might be profoundly modified by the change of temperature, and I accordingly carried out a number of experiments at zero. The results, contained in Tables 19 to 27, and in part in Fig. 2, show that, on the whole,

EXPTS. 19 AND 20.

19. *A*, 1.968; *B*, 237.9; *C*, 142.4; *V*, 100; k_{avg} , 0.0023; *R*, 0.063.
20. *A*, 0.984; *B*, 237.9; *C*, 142.4; *V*, 100; k_{avg} , 0.0022; *R*, 0.030.

19. θ	<i>x</i>	k_1	20. θ	<i>x</i>	k_1
10	0.66	0.0025	20	0.57	0.0022
15	0.86	0.0022	30	0.83	0.0022
20	1.19	0.0023	—	—	—
30	1.72	0.0023	—	—	—
∞	11.81	—	∞	5.90	—

EXPTS. 21, 22 AND 23.

21. *A*, 1.968; *B*, 478.3; *C*, 142.4; *V*, 100; k_{avg} , 0.012; *R*, 0.33.
22. *A*, 0.984; *B*, 478.3; *C*, 142.4; *V*, 100; k_{avg} , 0.013; *R*, 0.18.
23. *A*, 0.984; *B*, 235.3; *C*, 284.9; *V*, 100; k_{avg} , 0.0053; *R*, 0.072.

21. θ	<i>x</i>	$k_1 \times 10^4$	22. θ	<i>x</i>	$k_1 \times 10^4$	23. θ	<i>x</i>	$k_1 \times 10^4$
10	2.69	112	10	1.34	112	10	0.69	54
20	4.94	118	15	2.04	123	15	1.00	54
30	6.87	126	20	2.77	138	20	1.21	50
35	7.68	130	30	3.75	146	—	—	—
∞	11.81	—	∞	5.90	—	∞	5.90	—

TABLE 24.

A	B	C	Ex.	R(0°)	Ex.	R(30°)	Ratio	Coeff.
1.968	237.9	142.4	19	0.063	1	0.18	2.9	1.4
0.984	237.9	142.4	20	0.030	2	0.088	2.9	1.4
1.968	478.3	142.4	21	0.33	3	0.79	2.4	1.3
0.984	478.3	142.4	22	0.18	4	0.396	2.2	1.3
0.984	235.3	284.9	23	0.07-	5	0.26	3.6	1.5

EXPT. 25.

A, 17.79; C, 94.83 × n; V, 200; R corr. (30°) from Expt. 15.

B	n	θ	x	R corr.	R(30°)	Ratio	Coeff.
238.7	1	120	4.34	0.04	0.11	2.7	1.4
235.3	3	80	8.69	0.12	0.40	3.3	1.5
230.2	6	20	5.70	0.33	1.28	3.9	1.6
223.4	10	8	4.65	0.71	2.86	4.0	1.6

EXPT. 26.

A, 17.79; C, 94.83; V, 200; T, 0°C; R (30°) from Expt. 16.

B	θ	x	R	R(30°)	Ratio	Coeff.
238.7	120	4.34	0.04	0.11	2.7	1.4
479.2	40	5.73	0.15	0.42	2.7	1.4
960.0	10	7.41	0.81	1.83	2.3	1.3
1440.8	4	7.69	2.09	—	—	—

EXPT. 27.

A, 17.79 × n; B, 238.7; C, 94.83; V, 200; R (30°) from Expt. 17.

n	θ	x	R	R(30°)	Ratio	Coeff.
1	120	4.34	0.04	0.11	2.7	1.4
3	80	6.84	0.09	(0.26)	2.9	1.4
5	50	6.36	0.14	(0.40)	2.9	1.4
7	30	5.24	0.19	(0.63)	3.3	1.5
9	20	4.17	0.22	0.67	3.0	1.4

the effect of changing the concentrations of the various reagents is the same at zero as at thirty degrees; the iodide curve is flatter, and the acid curve a little steeper at the lower temperature.

Hence the temperature coefficient increases with C , and falls off when B is increased.

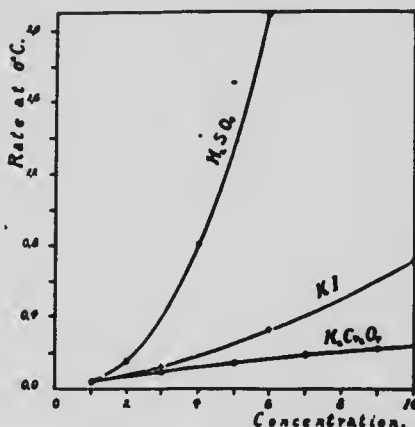


Fig. 2

Table 24 contains a résumé of the results of Expts. 19 to 23 with the rates at 30°, and the ratios of the two rates. The temperature-coefficient, that is, the cube root of this ratio, is entered under "coeff".

Cohen¹ gives a list of 16 reactions whose temperature coefficients have been measured; they vary from 3.6 to 1.9, all being much greater than that of the reaction studied in the present paper.

Summary

The rate of the reaction between potassium bichromate, potassium iodide, and sulphuric acid, is very nearly proportional to the concentration of the bichromate, and to the square of that of the acid.

The relation between the rate and the concentration of the iodide can be expressed by an equation of the form $R = mC + nC^2$.

The temperature coefficient of the reaction is unusually low.

¹ "Studien zur Chemischen Dynamik," (1895).

A number of salts which usually accelerate the process of oxidation have very little effect on the rate of this reaction. Exceptions are, ferric (and ferrous) salts, and, perhaps, chromic salts.

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

*University of Toronto,
February, 1903.*

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