LXII.—Catalysis. Part IV. Temperature Coefficients of Catalysed Reactions.

By NILRATAN DHAR.

In the foregoing paper it has been shown that although oxalic acid cannot reduce mercuric chloride even when boiled, the addition of a few drops of chromic acid and a trace of manganese salt is followed by the reduction of the chromic acid, and immediately thereafter by the reduction of mercuric chloride. It is the object of the present communication to throw light on the mechanism of this and other induced reactions, and, further, to study the temperature coefficients of reactions influenced by chemical catalysts or by light. The effect of change in the concentration of the reacting substances on temperature coefficients has also been investigated.

The investigation has covered the kinetics of the oxidation of oxalic acid and formic acid by chromic acid, and the oxidation of formates and oxalates by iodine, mercuric chloride, and silver nitrate.

EXPERIMENTAL.

Oxalic Acid and Chromic Acid.

Oxalic acid is slowly oxidised by chromic acid at the ordinary temperature, but at about 25° the velocity of the reaction is quite measurable.

Ordinary pure chromic acid was repeatedly washed with concentrated nitric acid in order to remove potassium salts. The washed specimen was dissolved in the minimum quantity of water and precipitated with concentrated nitric acid; this product was freed from nitric acid by heating it electrically in a vacuum desiccator over potassium hydroxide. The product was finally purified by recrystallisation from "conductivity water" and dried in a steam oven.

The ordinary pure oxalic acid was first crystallised from water to which were added a few drops of hydrochloric acid in order to decompose any sodium oxalate if present. This product was several times recrystallised from water and dried centrifugally.

Measured volumes of oxalic acid and chromic acid which had been previously brought to a constant temperature in a thermostat were rapidly mixed, and the time was noted. After definite intervals of time, measured quantities were withdrawn by means of calibrated pipettes. The unchanged chromic acid remaining was allowed to act on a mixture of potassium iodide and hydrochloric acid, and the iodine liberated was estimated with standard thiosulphate. The thiosulphate solution was prepared in distilled water freed from carbon dioxide and was about N/60.

The thermostat regulators used were spiral ones filled with toluene (Lowry type), and the Götze thermometers (divided into tenths) employed in the thermostats were checked against a normal thermometer which had been calibrated by the National Physical Laboratory.

Order of the Reaction.—The velocity of the reaction may be represented by an equation of the form $-dc_1/dt = kc_1^m c_2^n$, where c_1 and c_2 represent concentrations of chromic acid and oxalic acid respectively.

Determination of m.—In the following series of experiments the oxalic acid used was in large excess, and hence the concentration may be taken as practically constant during the course of the reaction; thus the velocity equation takes the following form: $-dc_1/dt = (kc_2^n)c_1^m = k_1c_1^m$, where $k_1 = kc_2^n$. The order of the reaction under the conditions specified is therefore the same as m.

Since the free chromic acid in the solution is equivalent to the amount of thiosulphate required, it is sufficient to give for each observation the amount of thiosulphate in c.c. The results recorded in the following four Tables were all obtained at 25° .

TAPLE I.

N/5-oxalic acid and N/100-chromic acid.

Time in minutes.	C.c. of Thiosulphate	$k_{\rm r} = 1/t \log c_{\rm r}/c_{\rm r}$
0	31·3	
8	21.7	0.0198
17	14.45	0.0197
33	6.95	0.0198
43.5	4.25	0.0199
70.5	1.25	0.0198
	Mean	0.0198

TABLE II.

3N/20-oxalic acid and N/100-chromic acid.

0	31.3	
20	20.5	0.00919
38	14.0	0.00919
50	10.9	0.00916
67	7.65	0.00913
89	4.9	0.00905

TABLE III.

N/10-oxalic acid and N/100-chromic acid.

Time in	C.c. of	
minutes.	Thiosulphate.	$k_1 = 1/t \log c_0/c.$
0	31.25	
23	25.6	0.00376
52	20.4	0.00356
91	15.2	0.00344
127	11.85	0.00332
167	9.1	0.00320

TABLE IV.

N/20-oxalic acid and N/100-chromic acid.

34.6	
27.8	0.000602
26.45	0.000592
21.95	0.000558
15.5	0.000515
10.25	0.000422
	$34.6 \\ 27.8 \\ 26.45 \\ 21.95 \\ 15.5 \\ 10.25$

It appears that, in spite of a slight tendency to fall off, the values of k_1 calculated for m=1 exhibit such a degree of constancy that the equation indicating a unimolecular reaction may fairly be regarded as the appropriate one. Hence, in the presence of a large excess of oxalic acid, the oxidation follows the unimolecular law.

Determination of n.—The method used was Ostwald's "isolation method." As remarked before, the constant k_1 involves the concentration of the oxalic acid in a manner expressed by the equation $k_1 = kc^n$, where k is the intrinsic velocity coefficient, c the concentration of oxalic acid, and n the number of oxalic acid molecules taking part in the reaction. Supposing that k_1' and k_1'' are the values of k_1 obtained in two experiments, in each of which the initial concentration of chromic acid is the same, whilst the concentrations of oxalic acid are different, say c'_2 and c''_2 , the following equations are obtained:

$$k_1' = kc_2'^n, k_1'' = kc_2''^n, \text{ whence } n = \log \frac{k_1'}{k_1''} / \log \frac{c_2'}{c_2''}$$

In using the measurements recorded in the foregoing Tables for the purpose of determining n, those values of k_1 are chosen where the amounts of unchanged chromic acid are approximately equal in the separate series. On comparing the Tables, the following results are obtained:

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It is evident that the values of k_1 decrease rapidly as the concentration of oxalic acid diminishes, which indicates a high value for the exponent *n*. The actual values of *n* calculated are 2.7 [from (1) and (2)], 2.65 [from (1) and (3)], 2.7 [from (1) and (4)], 2.65 [from (2) and (3)], 2.85 [from (2) and (4)], and 2.9 [from (3) and (4)]. It is seen that *n* approaches closely to the value 3, and the velocity coefficient k_1 varies, therefore, as the cube of the concentration of oxalic acid.

To sum up, the oxidation of oxalic acid by chromic acid is unimolecular with respect to chromic acid and termolecular with respect to oxalic acid, and consequently the whole reaction is quadrimolecular. The course of the change may accordingly be represented by the equation:

$$H_2Cr_2O_7 + 3H_2C_2O_4 = Cr_2O_3 + 4H_2O + 6CO_2.$$

The neutralisation of chromium oxide (Cr_2O_3) by oxalic acid is probably extremely rapid, and in this case would not affect the velocity of the reaction.

In order to study the effect of change in the concentration of chromic acid, further experiments were made at 25°, the results of which may be summarised as follows:

With N/4-oxalic acid.

Concentration of chromic acid	N/200	N/100	N/50
Value of k_1	0.0331	0.0317	0.0298

With 3N/20-oxalic acid

Concentration of chromic acid	N/250	N/200	N/50
Value of k_1	0.0106	0.0103	0.00837

It will be seen from the above figures that the value of the velocity coefficient k_1 appears to vary with the initial concentration of the chromic acid, becoming greater as the latter diminishes. This variation of k_1 cannot be ascribed either to varying ionisation or to any of the ordinary disturbing effects arising from the products of the reaction, since these would in general exert an influence during the course of the reaction, whereas the results recorded in Tables I to IV show that the value of k_1 is practically constant under these conditions. The coefficient is obviously affected by some factor which remains constant during a particular series of experiments, but varies from one series to another.

Since the velocity coefficients fall off as the concentration of chromic acid is increased, it does not appear justifiable to apply any of the methods for determining the order of the reaction

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which are based on varying dilution, since these assume that the velocity coefficient is intrinsically independent of concentration, whereas the course of the reaction may be disturbed by secondary Thus the well-known formula of Noyes, causes.

$$m = 1 + \log \frac{t_1}{t_2} / \log \frac{c_2}{c_1},$$

is derived by integration from the differential velocity equation $-dc/dt = kc^{m}$, on the assumption that the velocity k is independent of the concentration. In some subsequent experiments it will be shown that chromium salts, which are a product of the reaction, have practically no effect on the velocity. It has been assumed that the action of chromium oxide (Cr_2O_3) on oxalic acid is practically instantaneous. This would be the case if the oxalic acid were in very large excess; but when the oxalic acid is not in very large excess this neutralisation may have a definite velocity, which would affect the kinetics of the whole reaction, producing a retarding effect on the chemical change. This is probably the explanation of the fall in the velocity coefficient with the increase in the concentration of chromic acid.

In order to determine the temperature coefficient of the reaction, measurements were made at different temperatures. Typical examples of the results obtained are recorded in detail in Tables V and VI.

TABLE V.

At 25°.

N/10-oxalic acid and N/200-chromic acid.

Fime in	C.c. of	,
minutes.	Thiosulphate.	k_{1}
0	16.65	
43.25	11.25	0.00393
89	7.55	0.00386
130.25	5.35	0.00378
191	3.3	0.00368
248	2.05	0.00367
	Mean	0.00378
	TABLE VI.	
	TABLE VI. At 35°.	
0	TABLE VI. At 35°. 16·6	
$0 \\ 21 \cdot 15$	TABLE VI. At 35°. 16.6 11.35	0.00780
0 21·15 41	TABLE VI. At 35°. 16.6 11.35 8.15 8.15	0·00780 0·00753
0 21·15 41 73	TABLE VI. At 35°. 16.6 11.35 8.15 4.95	0.00780 0.00753 0.00719
0 21·15 41 73 90	TABLE VI. At 35°. 16.6 11.35 8.15 4.95 3.8	0.00780 0.00753 0.00719 0.00711
0 21·15 41 73 90 106	TABLE VI. At 35°. 16.6 11.35 8.15 4.95 3.8 3.05	0.00780 0.00753 0.00719 0.00711 0.00695

Hence temperature coefficient for 10° rise = $k_{t+10}/k_t = 1.94$.

The results of other measurements with oxalic and chromic acids at different temperatures are summarised below:

N/20-oxalic acid and N/200-chromic acid.

Temperature.	Mean k_1 .	k_{t+10}/k_t .
25°	0.000650	1.05
35°	0∙001269∫	1.20

3N/20-oxalic acid and N/200-chromic acid.

25°	0.0103)	1.02
35°	0∙0198 ∫	1.90

N/10-oxalic acid and N/100-chromic acid.

25°	0.00346 }	1.90
40°	0·00906 ¦	1.80
50°	0.0162	1.50
60°	0.0279 }	1.72

N/20-oxalic acid and N/100-chromic acid.

25°	0.000562	1.90
40°	0.00149	1.83
50°	0.00272	1.79
60°	0.00472	1.12

Applying the Arrhenius formula, $\log k_1/k_2 = A(T_1 - T_2)/T_1T_2$, to the results for (a) N/10-oxalic acid and N/100-chromic acid and (b) N/20-oxalic acid and N/100-chromic acid, we obtain the following results:

Temperature.	A = 2600		A = 2613	
	k (found).	k (calc.)	k (found).	k (calc.)
25°	(0.00346)	(0.00346)	(0.000566)	(0.000566)
40°	(0.00906)	(0·00906)	(0.00149)	(0.00149)
50°	`0·0163 ´	`0·0163 ´	0.00272'	0.00270
60°	0.0280	0.0281	0.00472	0.00476

The next point investigated was the effect of sulphuric acid on this reaction, and measurements were made at different temperatures with different concentrations of sulphuric acid. The following is a summary of the results obtained:

N/20-oxalic acid and N/100-chromic acid.

Concentration of H_2SO_4 k_1 at 25°	0 0.000562	$N/50 \\ 0.000796$	N/20 0.00105	$N/10 \\ 0.00128$
Concentration of H_2SO_4	N/5 0.00153	3 N/5	8 N/5	4/N
k_1 at 25°		0-00149	0.000890	0·000357

N/10-oxalic acid and N/100-chromic acid

Concentration of H ₂ SO ₄	0	N/5	7 N/2
k_1 at 25°	0.00346	0.00644	0.00140

Hence it appears that sulphuric acid at moderate concentrations accelerates the reaction, and in large excess retards it.

In order to determine the temperature coefficient of the oxidation of oxalic acid by chromic acid in the presence of sulphuric acid, measurements were made at 40° and 50° , and the following is a summary of the results:

3N/20-oxalic acid, N/100-chromic acid, and N/5-sulphuric acid.

Temperature.	Mean k_1 .	k_{t+10}/k_t
25°	0.01412	1.86
50°	0·0665 (1.00

N/10-oxalic acid, N/100-chromic acid, and N/5-sulphuric acid.

25°	0.00644	1.87
50°	0∙0309 ∫	1.01

N/20-oxalic acid, N/100-chromic acid, and N/10-sulphuric acid.

N/20-oxalic acid, N/100-chromic acid, and N/5-sulphuric acid.

 $\begin{array}{ccc} 25^{\circ} & & 0.00153 \\ 50^{\circ} & & 0.00699 \end{array} \right\} \quad 1.84$

The temperature coefficient of the oxidation of oxalic acid by chromic acid without sulphuric acid is 1.85. It appears, therefore, that the temperature coefficient remains unaltered in the presence of a small amount of sulphuric acid.

In order to determine the temperature coefficient in the presence of an excess of sulphuric acid, measurements were made at 40° . It has already been pointed out that in large excess, sulphuric acid acts as a negative catalyst in the oxidation of oxalic acid by chromic acid. The results are summarised as follows:

N/10-oxalic acid, N/100-chromic acid, and 7N/2-sulphuric acid.

Temperature	Mean k_1 .	k_{t+10}/k_t .
25°	0.00140	2.61
40°	0∙00591∫	2.01

N/20-oxalic acid and N/100-chromic acid.

Concentration of H ₂ SO ₄	0	3 N/5	8 N/5	4 N
$k_1 \text{ at } 40^{\circ}$	0.00149	0.00481	0.00318	0.00156
Temperature coefficient	1.90	2.18	$2 \cdot 34$	2.67

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From the foregoing results, it appears that in the presence of an excess of sulphuric acid the temperature coefficient is larger than that obtained in its absence, and the greater the concentration of the acid the greater is the value of the temperature coefficient.

Effect of Manganese Salts on the Oxidation of Oxalic Acid by Chromic Acid.

It has been observed that manganese salts markedly accelerate the oxidation of oxalic acid by chromic acid. A stock solution of recrystallised manganese sulphate was prepared and standardised by precipitating the manganese as carbonate by ammonium carbonate. The precipitate was allowed to remain at about 80° for two hours, then collected, heated in a porcelain crucible, and weighed as Mn_3O_4 . N/20-oxalic acid and N/100-chromic acid were used in each experiment with different amounts of manganese sulphate, and measurements were made at 25° .

TABLE VII.

0.03926 gram of MnSO₄ in 500 c.c.

a . .

Time in minutes.	thio- sulphate.	k_1 (unimolecular).	$k_{0}(x/t).$
0	31.3	/	
14	28.6	0.00279	0.20
43	$22 \cdot 1$	0.00351	0.21
75	15.95	0.00390	0.21
106	10.75	0.00437	0.20
138	$6 \cdot 2$	0.00509	0.18

TABLE VIII.

0.06544 gram of MnSO₄ in 500 c.c.

0	31.3		
15	26.6	0.00470	0.31
30	21.5	0.00544	0.32
50	15.25	0.00624	0.32
65	11.4	0.00675	0.31
85	6.6	0.00795	0.29

TABLE IX.

0.13088 gram of MnSO₄ in 500 c.c.

0	31.3		
11	25.35	0.00831	0.54
21	19.42	0.00987	0.56
31	14.1	0.01117	0.56
41	9.35	0.01280	0.54
52	4 ·8	0.01566	0.51

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TABLE X.

0.19632 gram of MnSO₄ in 500 c.c.

Time in minutes.	C.c. of thio- sulphate.	k_1 (unimolecular).	$k_0 (x/t).$
0	31.3		
9	24.75	0.01132	0.73
17	17.95	0.01420	0.78
25	11.9	0.01680	0.77
31	8.1	0.01893	0.75
37	4.8	0.02208	0.72

Assuming that the velocity is proportional to the concentration of manganese sulphate, the course of the reaction may be represented by the equation

$$-dc_1/dt = kc_1^m c_2^n \cdot h_2$$

where c_1 and c_2 represent the concentrations of chromic acid and oxalic acid respectively and h represents the concentration of manganese sulphate. If the concentration of oxalic acid is made large compared with that of chromic acid, the concentration of the former does not sensibly alter during the course of the reaction, and the equation takes the form

 $-dc_1/dt = (kc_2^n)c_1^m h = k_1 c_1^m,$

where $k_1 = h \cdot kc_2^n$; if m = 1, the reaction would be unimolecular, and on integrating we get $k_1 = 1/t \log c_0/c_1$, and, as a matter of fact, in the absence of manganese sulphate the reaction is unimolecular, as previously shown. If, on the other hand, m = 0, the expression becomes $-dc_1/dt = k_1$ or $c_1/t = k_1$, that is, if the velocity of the reaction were independent of the concentration of chromic acid, we should have $c_1/t = \text{const.}$ or $x/t = k_0$, where x = difference in the thiosulphate readings.

In the foregoing Tables, the unimolecular coefficient and this new coefficient (x/t = const.) are both set out, and it is seen that the unimolecular coefficient, far from being constant, increases notably with the time, whilst this new coefficient is almost constant. Hence it appears that in the presence of manganese sulphate, the velocity of the oxidation is independent of the concentration of chromic acid.

Homogeneous reactions in which the velocity is independent of the concentration of one of the reacting substances are of rare occurrence. One case is described by Friend (T., 1906, **89**, 1096), who studied the reaction between hydrogen peroxide and potassium persulphate and found that the velocity was independent of the concentration of the peroxide provided the latter was present in large excess. Another case has been investigated by Steele (T.,

1907, 91, 1641), who found that in the oxidation of hypophosphorous acid by iodine in the presence of hydrogen ions the reaction-velocity is independent of the iodine concentration. Such behaviour is usually attributed to complications due to the occurrence of consecutive reactions, and in the present case it appears that the reaction occurs in two stages, one very much faster than the other, and that the chromic acid does not take part in the slower or controlling reaction (compare Skrabal, Zeitsch. anorg. Chem., 1904, 42, 1; Jablczyński, ibid., 1908, **60**, 38).

Although from the experiments recorded above it appears that the velocity of the oxidation of oxalic acid by chromic acid in the presence of manganese sulphate is independent of the concentration of chromic acid, yet, when the concentration of manganese sulphate is exceedingly small, the reaction appears to be The following Tables will indicate the results unimolecular. obtained with very small concentrations of manganese sulphate.

N/20-oxalic acid and N/100-chromic acid at 25° with

TABLE XI.				TABLE X	II.
(a) 0.00393 gram of MnSO ₄ in 500 c.c.			(b N) 0 [.] 00262 g InSO ₄ in 50	ram of 00 c.c.
Time in minutes.	C.c. of thio- sulphate.	k_1 (uni- molecular).	Time in minutes.	C.c. of thio- sulphate.	kı (uni- molecular).
0	31.3		0	31.3	
138	$27.3 \\ 24.4$	0.000790	160	$27 \cdot 2 \\ 24 \cdot 2$	0.000708
188	22.4	0.000773	240	21.5	0.000679
245	20.35	0.000763	356	18.35	0.000651

In the following experiments, the joint effect of both sulphuric acid and manganese sulphate was studied at 25°.

N/20-oxalic acid, N/100-chromic acid, and N/20-sulphuric acid.

With 0.06544 gram of MnSO ₄ in 500 c.c.			With 0.01309 gram of MnSO4 in 500 c.c.				
$\begin{array}{c} 0 \\ 10 \\ 30 \\ 45 \\ 63 \\ 95 \end{array}$	$ \begin{array}{r} 33.6 \\ 30.2 \\ 21.0 \\ 14.95 \\ 8.95 \\ 2.0 \end{array} $	0.00463 0.00680 0.00781 0.00911	$ \begin{array}{c} 0.34 \\ 0.42 \\ 0.41 \\ 0.40 \\ 0.26 \\ \end{array} $	$ \begin{array}{c} 0 \\ 15 \\ 37 \\ 72 \\ 132 \end{array} $	$33 \cdot 6$ $31 \cdot 35$ $28 \cdot 2$ $23 \cdot 6$ $17 \cdot 0$	$\begin{array}{c} &$	$0.15 \\ 0.15 \\ 0.14 \\ 0.13$

Hence, even in the presence of sulphuric acid the reaction velocity is independent of the concentration of chromic acid.

In order to determine the temperature coefficient of the oxida-

tion of oxalic acid by chromic acia in the presence of manganese sulphate, measurements were made at various temperatures.

N/20-Oxalic acid and N/100-chromic acid were used in each experiment with different quantities of manganese sulphate.

TABLE XV.

With 0.02617 gram of $MnSO_4$ in 500 c.c.

	\mathbf{At}	25°.			At	40°.	
Time	C.c.	k_1		Time	C.c.	k_1	
in	of thio-	(unimole-		\mathbf{in}	of thio-	(unimole-	
minutes.	sulphate.	cular).	$k_0(x/t)$.	minutes.	sulphate.	cular).	$k_0(x/t)$.
0	33.3			0	33.3	-	
20	30.28	0.00206	0.15	8	27.27	0.0108	0.75
50	25.0	0.00249	0.16	18	19.95	0.0123	0.74
78	20.65	0.00265	0.16	27	14.2	0.0137	0.71
115	15.35	0.00292	0.16	35	9.68	0.0153	0.68
144	10.4	0.00351	0.16	45	$4 \cdot 9$	0.0184	0.64
	I	Mean	0.16			Mean	. 0.70

Therefore $k_{t+10}/k_t = 2.67$.

TABLE XVI.

With 0.7050 gram of $MnSO_4$ in 500 c.c.

At 0°.					At 2	5°.	
Time	C.c.	k_1		Time	C.c.	k_1	
in	of thio-	(unimole-		in	of thio-	(unimole-	
minutes.	sulphate.	cular).	$k_0(x/t)$.	minutes.	sulphate.	cular).	$k_0(x/t)$.
0	33.3	'		0	33.3		
60	26.9	0.00154	0.107	4	27.5	0.0207	1.45
120	19.3	0.00195	0.117	12	12.65	0.0320	1.72
175	14.05	0.00214	0.110	16	7.8	0.0394	1.60
225	10.9	0.00215	0.100	20	4 ·8	0.0420	1.42
275	8.0	0.00225	0.092		—		
	М	ean	$\overline{0.105}$		М	ean	1.55

Therefore k_{t+10}/k_t between 0° and 25° = 2.93.

As has been previously observed, in the presence of manganese sulphate the oxidation of oxalic acid by chromic acid is independent of the concentration of the latter. Hence the reaction becomes of an order lower than that of the reaction in the absence of manganese salts. It is well known that reactions in which one or two molecules take part have larger temperature coefficients than those of reactions of higher order (compare Halban, Zeitsch. physikal. Chem., 1909, **67**, 129).

The temperature coefficient of the oxidation of oxalic acid by chromic acid is 1.94 between 25° and 40° , whilst in the presence of manganese salts it is 2.68 between 25° and 40° and 2.95 between 0° and 25° , agreeing with other known examples.

Effect of Other Catalysts on the Oxidation of Oxalic Acid by Chromic Acid.

Summary of results obtained with N/10-oxalic acid and N/100chromic acid and different concentrations of molybdic acid:

Concentra	non	or mory	puic				
acid	•••			0	0.0063	0.0082	0.01367
k_1 at 25°	•••		•••	0.00353	0.00173	0.00145	0.00086
Temperat	ure c	oefficien	t	1.92	1.99	$2 \cdot 0$	2.05

From the above figures it appears that the negative catalyst, molybdic acid, produces an increase in the value of the temperature coefficient.

Summary of results obtained with ammonium molybdate as a catalyst with N/10-oxalic acid and N/100-chromic acid:

Molar concentration	\mathbf{of}				
molybdate	•••	0	0.000463	0.000926	0.002315
k_1 at 25°	•••	0.00353	0.00245	0.00180	0.000766
Temperature coefficient	•••	1.92	1.99	2.01	2.08

Summary of results with boric acid as a catalyst with N/10-oxalic acid and N/100-chromic acid:

(1	4	- 6
Concer	uration	- OI

boric acid \dots k_1 at 25° \dots	0 0·00353	$0.01434 \\ 0.00343$	0·0358 0·00317	0·0716 0·00283	0·216 0·00207	$0.432 \\ 0.00138$
coefficient	1.92	1.95	1.99	$2 \cdot 0$	2.11	2.24

Both ammonium molybdate and boric acid are retarders. The greater the retardation the greater is the value of the temperature coefficient.

Formic Acid and Chromic Acid.

Formic acid can also be oxidised by chromic acid; at equal concentrations the velocity of the oxidation of formic acid is decidedly smaller than that of the oxidation of oxalic acid. Hence, in measuring the velocity at 25°, fairly concentrated solutions of formic acid have been used. The experimental method is the same as in the oxalic acid oxidation; since formic acid is volatile, especially at the higher experimental temperatures, tightly fitting stoppered Jena-glass bottles were used as reaction vessels. Kahlbaum's pure formic acid was used throughout the measurements. From a concentrated stock solution of 15 litres, suitably diluted solutions were prepared. In this case, also, the free chromic acid in the reaction mixture was estimated from time to time by the iodometric method, and the amounts of sodium thiosulphate required are recorded in the tables. From comparative experiments it was first established that the presence of free formic acid or oxalic acid did not interfere with the accuracy of the estimation of chromic acid by the iodometric method; as a rule, in the estimation of chromic acid by this method, an excess of hydrochloric acid was used, and the velocity of the oxidation of formic or oxalic acid by iodine, especially in the presence of hydrochloric acid, is negligible. The velocity of the reaction may be represented by the equation $-dc_1/dt = kc_1^m c_2^n$, where c_1 and c_2 denote concentrations of chromic and formic acids respectively.

Determination of m.—In the following series of experiments, the formic acid used was in large excess, and hence the concentration may be taken as practically constant during the course of the reaction; the velocity equation takes the following form: $-dc_1/dt = (kc_2^n)c_1^m = k_1c_1^m$, where $k_1 = kc_2^n$. Hence the order of the reaction is the same as m.

The results recorded in the following Tables were all obtained at 25° .

TABLE I.

6.166 N-formic acid and N/30-chromic acid.

	C.c. of	
Time in	thio -	
minutes.	sulphate.	$k_1 = 1/t \log c_0/c_0$
0	$52 \cdot 1$	
95	26.55	0.00308
135	19.95	0.00309
200	12.6	0.00308
275	7.4	0.00308
330	5.0	0.00308

Mean..... 0.00308

TABLE III.

2.466 N-formic acid and N/30-chromic acid.

0	56.1	
240	49.0	0.000245
475	42.9	0.000245
1345	26.6	0.000241
1907	19.0	0.000247

Mean..... 0.000245

TABLE V.

5.933 N-formic acid and N/30-chromic acid.

0	56.1	_
83	33.0	0.00277
130	24.75	0.00273
170	19.2	0.00274
227	13.3	0.00275
	Mean	0.00275

TABLE II.

3.083 N-formic acid and N/30-chromic acid.

	C.c. of	
Time in	\mathbf{thio} -	
minutes.	sulphate.	k_1 .
0	$52 \cdot 1$	_
135	45.15	0.000460
285	38.5	0.000460
525	29.65	0.000466
1416	11.55	0.000462
1817	7.6	0.000460

Mean..... 0.000462

TABLE IV.

2.966 N-formic acid and N/30-chromic acid

0	$55 \cdot 4$	
155	47.8	0.000413
335	40.25	0.000412
555	$32 \cdot 8$	0.000410
1360	$15 \cdot 2$	0.000413

Mean..... 0.000412

TABLE VI.

2.3733 N-formic acid and N/30-chromic acid.

0	56.1	
247	49.5	0.000220
504	$43 \cdot 4$	0.000221
1450	27.0	0.000219
1990	20.45	0.000220
	Mean	0.000220

From the foregoing results it appears that the values of k_1 calculated for m=1 exhibit such a degree of constancy that the equation indicating a unimolecular reaction may fairly be regarded as the appropriate one. Hence, in the presence of an excess of formic acid, the oxidation is a unimolecular reaction.

Determination of n.—The "isolation method" is also used in this oxidation. Supposing that k_1' and k_1'' are the values of k_1 (in the equation $k_1 = kc^n$) obtained in two experiments, in each of which the initial concentration of chromic acid is the same, whilst the concentrations of formic acid are different, say c_2' and c_2'' , the following equations are obtained: $k_1' = kc_2'^n$, $k_1'' = kc_2''^n$, whence

$$n = \log \frac{k_1'}{k_1''} \bigg/ \log \frac{c_{9}'}{c_{9}''}.$$

On comparing the Tables I—VI, the following results are obtained:

Cl		(1)	(2)	(3)	(4)	(5)	(6)
formic acid	01 	6.166	3.083	$2 \cdot 466$	2.966	5.933	2.373
$k_1 { m at} 25^\circ \dots$		0.00308	0.000462	0.000245	0.000412	0.00275	0.000220

It is evident that the value of k_1 decreases rapidly as the concentration of formic acid diminishes, which indicates a high value for the exponent *n*. The actual values of *n* obtained by combining these results are 2.7, 2.8, 2.75, 2.96, 2.8, 2.85, 2.96, 2.75, 2.84, 2.75, 2.8, 2.75, 2.8, and 2.76. It is seen that *n* approaches closely to the value 3, and the velocity coefficient k_1 varies, therefore, as the cube of the concentration of formic acid.

To sum up, the oxidation of formic acid also is unimolecular with regard to chromic acid and termolecular with respect to formic acid, and consequently the whole reaction is quadrimolecular. The course of the change may accordingly be represented by the equation

$$\mathbf{H}_{2}\mathbf{Cr}_{2}\mathbf{O}_{7} + \mathbf{3H} \cdot \mathbf{CO}_{2}\mathbf{H} = \mathbf{Cr}_{2}\mathbf{O}_{3} + \mathbf{6H}_{2}\mathbf{O} + \mathbf{3CO}_{2}.$$

The action of chromium oxide (Cr_2O_3) on formic acid may be assumed to be extremely rapid and to be without effect on the velocity of the reaction. From the kinetic measurements it is seen that only one molecule of chromic acid takes part in the reaction, and consequently these measurements support the view that the formula of chromic acid is $H_2Cr_2O_7$ and not H_2CrO_4 ; had it been H_2CrO_4 , two molecules of chromic acid should have taken part in the reaction (compare Datta and Dhar, J. Amer. Chem. Soc., 1916, **38**, 1303).

In order to study the effect of change in the concentration of chromic acid, further experiments were made at 25°, the results of which may be summarised as follows: With 3.083 N-formic acid.

Concentration of chromic acid	N/15	N/30	N/60
$k_1 ext{ at } 25^{\circ} \dots$	0.000461	0.000462	0.000462

With 2.966 N-formic acid.

 Concentration of chromic acid...
 N/30 N/60

 k_1 at 25°
 0.000413 0.000412

Hence in this reaction, if we use an excess of formic acid and vary the concentration of chromic acid, we find that the unimolecular coefficient does not change with the chromic acid concentration. In the presence of an excess of formic acid, therefore, the reaction is strictly unimolecular and there are no disturbing factors.

In order to determine the temperature coefficients of the reaction, measurements were made at different temperatures. Typical examples of the results obtained are recorded in detail in Tables VII, VIII, and IX.

TABLE VII.

2.966 N-Formic acid and N/30-chromic acid were used in each experiment:

At 40°.

t.	a-x.	k_1 .	
0	57.1		
105	42.3	0.00124	
195	32.5	0.00125	
300	24.5	0.00122	Table IV gives k_1 at $25^\circ = 0.000412$.
425	17.25	0.00122	Therefore $k_{t+10}/k_t = 2.07$.
495	14.05	0.00123	

Mean..... 0.00123

TABLE VIII.

At 50°.

0	55.35		
40	43.95	0.00256	
90	33.0 5	0.00248	From Tables VII and VIII we get
152	$22 \cdot 85$	0.00252	k_{t+10}/k_t between 40° and 50° =
214	16.35	0.00250	2.02.
266	12.0	0.00250	

Mean..... 0.00250

TABLE IX.

At 60°.

0	57.0		
37	37.7	0.00485	
71	25.9	0.00482	From Tables VIII and IX we get
105	17.95	0.00477	k_{t+10}/k_t between 50° and 60°=
153	10.7	0.00474	1.9.

Mean..... 0.00479

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Applying the Arrhenius formula $\log k_1'/k_1'' = A \cdot (T_1 - T_2)/T_1T_2$, we get the value of A = 3015.

Temperature.	k_1 (obs.).	k1 (calc.).
25°	(0.000412)	(0.000412)
40°	0.00123	0.000125
50°	(0.00250)	(0.00250)
60°	0.00479	0.00476

In order to study the effect of change in the concentration of formic acid on the temperature coefficient, measurements were made with different concentrations of formic acid and N/30-chromic acid, and the results obtained are summarised below:

5-933 N-formic acid	Temperature interval Temperature	2540° 2.05	4060°	
	(coefficient	2.03	1.91	
3·083 <i>N</i> -formic acid	Temperature interval Temperature coefficient	25 35° $2\cdot09$	25—50° 2∙03	
2.966 N-formic acid	Temperature interval Temperature coefficient	25—40° 2·07	40—50° 2∙02	50—60° 1∙90
1·186 N-formic acid	Temperature interval Temperature		40—50°	50—60°
	coefficient		2.01	1.90

From the above figures it appears that change in the concentration of formic acid has no appreciable effect on the temperature coefficient.

Effect of Sulphuric Acid.—The effect of sulphuric acid was studied at various temperatures with different concentrations of the acid. Typical examples of the results obtained are recorded in Table X.

TABLE X.

3.083 N-Formic acid, N/30-chromic acid, and N/6-sulphuric acid.

	At 25° .	•		At 50°.	
t.	a - x.	k_1 .	t.	a - x.	k_1 .
0	55.9		0	55.9	
117.5	40.4	0.00120	24	40.8	0.00570
219	30.8	0.00118	44.3	$31 \cdot 2$	0.00572
350	$21 \cdot 6$	0.00118	60	$25 \cdot 4$	0.00571
462	15.6	0.00120	90	17.1	0.00571
	Mean	0.00119		Mean	0.00571

Therefore $k_{t+10}/k_t = 1.87$.

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Summary of results obtained with 3.083 N-formic acid and N/30-chromic acid:

Concentration of H_2SO_4 k. at 25°	0 0.000462	N/6 0.00119	$N/3 \\ 0.00262$	$\frac{2N/3}{0.00603}$
Temperature coefficient be-				
tween 25° and 50°	2.03	1.87	1.86	1.84

From the foregoing results it appears that in the presence of sulphuric acid the oxidation of formic acid by chromic acid is greatly accelerated and has a lower value for its temperature coefficient, and the greater the concentration of sulphuric acid the greater is the fall. Experiments were made with other concentrations of formic acid, using sulphuric acid as an accelerator. A summary of the results obtained will be found in the following Tables. In each case N/30-chromic acid was used.

TABLE XI.

a ,

	Concentra-			
Concentra- tion of formic acid.	tion of sulphuric acid.	$\begin{array}{c} \operatorname{Mean} k_1 \\ \operatorname{at} 25^\circ. \end{array}$	$\begin{array}{c} \text{Mean} \ k_1 \\ \text{at} \ 50^\circ. \end{array}$	k_{t+10}/k_t
1.233 N	0	0.000055	0.000330	2.04
1.233 N	N/6	0.000348	0.00162	1.85
1.233 N	N'/3	0.000766	0.00356	1.84
1.233 N	$3\dot{N}/5$	0.00161	0.00724	1.83
0.616 N	0	0.0000092	0.000055	2.04
0.616 N	N/6	0.000144	0.000673	1.85
0.616 N	N/3	0.000320	0.00148	1.84
0.616 N	$2\dot{N}/3$	0.000748	0.00340	1.83

TABLE XII.

Concentra- tion of formic acid.	Concentra- tion of sulphuric acid.	$\begin{array}{c} \text{Mean} \ k_1 \\ \text{at} \ 25^\circ. \end{array}$	$\begin{array}{c} \text{Mean } k_1 \\ \text{at } 40^\circ. \end{array}$	k_{t+10}/k_t
1·186 N	0	0.0000515	0.000154	2.07
1.186 N	N/5	0.000304	0.000802	1.91
1.186 N	$3\dot{N}/5$	0.00122	0.00317	1.89
1.186 N	6N'/5	0.00373	0.00948	1.85
0.593 N	0 '	0.0000084	0.0000251	2.07
0.593 N	N/3	0.000253	0.000662	1.90
0.593 N	$19\dot{N}/15$	0.00112	0.00291	1.88

From all these results it is seen that there is a slight fall in the temperature coefficient with the increase in the concentration of sulphuric acid.

The next point investigated was the effect of manganese sulphate on the oxidation of formic acid by chromic acid. From qualitative experiments it was observed that manganese salt was a retarder in this reaction, whilst it had been previously shown that it is a great accelerator in the oxidation of oxalic acid by chromic acid.

TABLE XIII.

At 50°.

6.166 N-Formic acid, N/30-chromic acid, and 0.000164 gram of MnSO₄. Volume of mixture = 150 c.c.

t.	a-x.	k_1 .
0	51.8	
20	28.08	0.0133
39	15.8	0.0132
77	4.85	0.0133
87	3.6	0.0133

Mean..... 0.0133

 k_1 at 50° without any manganese sulphate = 0.0177; hence this reaction is very susceptible to the retarding influence of manganese sulphate even in very small concentration. The following is the summary of results obtained with 6.166 N-formic acid and N/30-chromic acid at 50° with different concentrations of manganese sulphate:

From the summary, it is seen that the greater the amount of manganese sulphate the greater is the retardation.

The following is the summary of results obtained with 3.083 N-formic acid and N/30-chromic acid at 50° :

Gram of MnSO4	0	0.0000164	0.000164	0.00164
k ₁ at 50°	0.00272	0.00264	0.00225	0.00154

Hence it is seen that the oxidation of formic acid by chromic acid is extremely sensitive to the retarding influence of manganese sulphate, so much so that 0.0000164 gram of manganese sulphate in 150 c.c. appreciably affects the velocity coefficients.

In order to determine the temperature coefficient of the oxidation of formic acid by chromic acid in the presence of manganese sulphate, experiments were made at several temperatures. Typical results are given in the following Table.

TABLE XIV.

3.083 N-Formic acid, N/30-chromic acid, and 0.02617 gram of MnSO₄. Volume of mixture = 150 c.c.

	At 25°.			At 35°.	
t. 0 385 1366 1610 1815 2870	a-x. 44.0 37.15 24.3 21.88 19.95 12.50	$\begin{array}{c} k_1. \\ 0.000190 \\ 0.000189 \\ 0.000188 \\ 0.000188 \\ 0.000189 \\ 0.000189 \end{array}$	t. 0 190 380 1395 1675	a - x. 54.75 45.9 38.7 15.2 11.8	$\begin{array}{c} k_1. \\ 0.000403 \\ 0.000396 \\ 0.000398 \\ 0.000397 \end{array}$
	Mean	0.000189		Mean	0.000398

Therefore $k_{t+10}/k_t = 2.10$; the temperature coefficient without any manganese salt is 2.09. Hence in the presence of manganese sulphate the temperature coefficient remains unaltered. The following is a summary of the results obtained with 6.166 N-formic acid and N/30-chromic acid with different concentrations of manganese sulphate:

Gram of MnSO ₄ k_1 at 25°	0 0·00308	$0.0654 \\ 0.00115$	0·0819 0·00112	0·3272 0·00106
Temperature coefficient between 25° and 50°	2.03	2.03	$2 \cdot 03$	2.03

The following Table summarises the results obtained with 2.966 N-formic acid and N/30-chromic acid with greater concentrations of manganese sulphate.

TABLE XV.

Grams of	Mean k_1	Mean k_1	
MnSO4.	at 25°.	at 50°.	k_{t+10}/k_t
0	0.000413	0.00250	2.05
1.1750	0.000141	0.000841	2.04
1.7625	0.000122	0.000734	2.05
2.3500	0.000136	0.000809	2.04
3.5250	0.000138	0.000810	2.03
5.8750	0.000142	0.000860	2.05
11.7500	0.000172	0.000970	$2 \cdot 0$

It appears from the foregoing results that the temperature coefficient in the presence of the negative catalyst, manganese sulphate, does not change. Also it is seen that if the concentration of manganese sulphate is increased, the velocity coefficient falls off to a certain limiting value and then increases with the increase in the concentration of the catalyst.

The joint effect of sulphuric acid and manganese sulphate on the oxidation of formic acid by chromic acid was also investigated at 50°.

TABLE XVI.

1.233 N-Formic acid and N/30-chromic acid. Volume of mixture=150 c.c.

(a) With 0.01309 gram of $MnSO_4$.			(b) With 0.01309 gram of $MnSO_4$ and $N/3$ -sulphuric acid.		
t.	a - x.	k_1 .	t.	a - x.	k_1 .
0	55.6		0	55.6	<u> </u>
406	46.9	0.000182	41	47.35	0.00170
1445	30.5	0.000180	121	34.65	0.00170
1920	$25 \cdot 1$	0.000180	265	20.0	0.00168
3025	15.85	0.000180	331	15.25	0.00168
4325	9.1	0.000182	413	11.2	0.00169
]	Mean	0.000181		Mean	0.00169

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 k_1 without any sulphate = 0.000330, whilst k_1 with N/3-sulphuric acid but no manganese sulphate = 0.00356. Consequently even in the presence of the accelerator, sulphuric acid, manganese sulphate has a retarding effect.

Next, the effect of manganese chloride was studied. The salt was purified by crystallisation from water. The following is a summary of the results obtained with manganese chloride as a catalyst and 3.083 N-formic acid and N/30-chromic acid:

Concentration of $MnCl_2$	0	0.0018	0.0090	0·0179	$0.0359 \\ 0.000169$
k_1 at 25°	0·000462	0.000205	0.000190	0·000179	
between 25° and 40°	2.06	2.10	2.11	$2 \cdot 12$	2.14
Concentration of $MnCl_2$	0·0718	0·1795	0·359	0·718	
k_1 at 25°	0·000164	0·000180	0·000207	0·000300	
between 25° and 40°	$2 \cdot 14$	$2 \cdot 16$	$2 \cdot 15$	$2 \cdot 14$	

Hence manganese chloride, like manganese sulphate, even in dilute solutions, produces a marked retarding effect on this reaction. If the concentration of the manganese salt is increased, the velocity coefficient falls off to a minimum and then increases with the increase in the concentration of the catalyst. This peculiar behaviour of the catalyst in fairly dilute solutions (for example, the maximum concentration used is 0.718 N) is seldom encountered (compare Tubandt, *Annalen*, 1905, **339**, 41; 1907, **354**, 259; 1910, **377**, 284).

Moreover, it will be seen from the foregoing summary that the temperature coefficient in the presence of the negative catalyst is appreciably higher than that obtained without any manganese chloride.

It is known that molybdic acid is a powerful catalyst in some oxidations, and its effect on this reaction was studied, N/30-chromic acid being used in each experiment.

Concentra-	Molar con- centration			
tion of	of molybdic	Mean k_1 at 25°	Mean k_1 at 40°	$k_{\ell+10}/k_{\ell}$.
2.966N	0	0.000412	0.00123	2.07
	0.002	0.000416	0.00125	2.08

Hence molybdic acid acts as a weak positive catalyst on the oxidation of formic acid by chromic acid, whilst it has been shown previously that in the oxalic acid oxidation it is a negative catalyst.

Sodium Formate and Iodine.

Formates are easily oxidised by iodine at the ordinary temperature, and this reaction has a conveniently measurable velocity. The course of the reaction is represented by the equation:

 $\mathbf{H} \cdot \mathbf{CO}_2 \mathbf{Na} + \mathbf{I}_2 = \mathbf{NaI} + \mathbf{HI} + \mathbf{CO}_2.$

The hydrogen ions formed as a product of the change greatly retard the reaction, and in order to avoid their formation an excess of a salt of a weak acid (for example, sodium acetate) was always used; in this way the course of the reaction became regular.

Ordinary pure iodine was mixed with a little potassium iodide and was allowed to sublime very slowly. This product was again sublimed. Schuchardt's pure sodium formate was recrystallised from water. A standard solution was prepared by evaporating a measured volume of the solution in a platinum crucible, heating the residue with sulphuric acid, and weighing the sodium sulphate formed. The potassium iodide used was twice crystallised from water and dissolved in water free from oxygen. The solution of the iodide was standardised by weighing the silver iodide obtained from a known volume of the solution.

In order to avoid loss of iodine by volatilisation, tightly fitting stoppered Jena-glass bottles were used as reaction vessels. From time to time measured volumes were withdrawn from the reaction vessel, which was placed in a thermostat at a constant temperature, and were allowed to run into ice-cold distilled water to stop the reaction, and the free iodine was immediately titrated by standard thiosulphate. The velocity of the reaction may be represented by the equation $-dc_1/dt = kc_1^m c_2^n$, where c_1 and c_2 are the concentrations of iodine and formate respectively. Since iodine dissolves very sparingly in water, in order to prepare a moderately concentrated solution potassium iodide must be used. It is well known that in a potassium iodide solution of iodine there is the following equilibrium, $KI_3 \rightleftharpoons KI + I_2$, and the greater part of the dissolved iodine exists as KI3. Hence, even if a large excess of sodium formate in comparison with the total iodine is not used, owing to the presence of potassium iodide, the concentration of free iodine is much diminished, and the concentration of formate is actually large in comparison with that of free iodine. Consequently the velocity equation takes the following form: $-dc_1/dt = (kc_2^n)c_1^m = k_1c_1^m$, where $k_1 = kc_2^n$. The order of the reaction is therefore the same as m.

In the three following Tables 1.27 grams of iodine and 5.4132 grams of potassium iodide were used with different concentrations of sodium formate, and the measurements were made at 25° ; the total volume of the mixture was 150 c.c.

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TABLE I.

3.4004 Grams of sodium formate. 1.7002 Grams of sodium formate.

TABLE II.

Time in minutes.	C.c. of thio- sulphate.	$k_1 = 1/t \log c_0/c$.	Time in minutes.	C.c. of thio- sulphate.	$k_1 = 1/t \log c_0/c.$
0	76.0		0	79.0	
24	68.0	0.00201	45	71.1	0.00101
60	57.6	0.00201	115	60.6	0.00100
91	49.65	0.00203	188	51.95	0.00097
141	41 ·0	0.00190	279	43.5	0.00093
174	36.1	0.00186	360	37.4	0.00090
			509	28.7	0.00086
I	Mean	0.00196		M ean	0.000945

TABLE III.

0.6801 Gram of sodium formate.

0	79.0	
100	72.3	0.000385
250	63.3	0.000384
480	51.9	0.000380
440	$23 \cdot 15$	0.000370
	M ean	0.000380

In all these measurements 4.22 grams of sodium acetate were used in each experiment. In the Tables IV, V, VI, and VII 0.635 gram of iodine and 2.7006 grams of potassium iodide were used in each observation at 25° with different concentrations of sodium formate, and the total volume was always 150 c.c.

TABLE IV.

TABLE V.

6.8008 Grams of sodium formate. 3.4004 Grams of sodium formate.

	Mean	0.00781		Mean	0.00378
78	10.65	0.00729	130	13.6	0.00356
52	15.85	0.00762	106	$16 \cdot 2$	0.00365
25	24.75	0.00812	71	$21 \cdot 2$	0.00380
10	32.7	0.00821	30	29.7	0.00412
0	39.5		0	39.5	

TABLE VI.

TABLE VII. 1.7002 Grams of sodium formate. 0.6801 Gram of sodium formate.

0	39.5		0	39.5	
50	31.5	0.00196	100	32.93	0.000790
100	25.3	0.00193	200	27.7	0.000770
140	21.5	0.00188	390	20.0	0.000758
201	17.15	0.00180	520	16-1	0.000750
285	12.6	0.00174			
		·			<u> </u>
	Mean	0.00186	ļ	Mean	0.000767

From the foregoing Tables it is seen that, in spite of a slight tendency to fall off, the values of k_1 calculated for m=1 exhibit such a degree of constancy that the equation indicating a unimolecular reaction may fairly be regarded as the appropriate one.

Determination of n.—Supposing that k_1' and k_1'' are the values of k_1 (in the equation $k_1 = kc^n$) obtained in two experiments, in each of which the initial concentration of iodine is the same, whilst the concentrations of sodium formate are different, say c_2' and c_2'' , the following equations are obtained: $k_1' = kc_2''n$; $k_1'' = kc_2''n$, whence $n = \log \frac{k_1'}{k_1''} / \log \frac{c_2'}{c_2''}$. On comparing the foregoing Tables, the following summary of results is obtained:

٨	
Δ	٠

Grams of formate	3.4004	1.7002	0.6801	$\int_{iodine}^{1\cdot27} \text{ grams of} \\ \text{findine and } 5\cdot4132$
k_1 at 25°	0.00196	0.000945	0.000380	grams of potass- ium iodide.

В.

Grams of formate	6.8008	3.4004	1.7002	0.6801	iodine and 2.7066
k_1 at 25 [°]	0.00781	0.00378	0.00186	0.000767	grams of potass- ium iodide.

The actual values of n obtained in A are 1.05, 1.02, and 0.99, and from B the values are 1.04, 1.03, 1.01, 1.02, 0.99, and 0.97. It is seen that n approaches closely to the value 1, and the velocity coefficient k_1 varies, therefore, directly as the concentration of sodium formate.

To sum up, the oxidation of sodium formate by iodine is unimolecular with respect to both iodine and sodium formate, and consequently the reaction is bimolecular; this behaviour is expected from the chemical equation representing the change $H \cdot CO_2Na + I_2 = HI + NaI + CO_2$.

From the foregoing summary of results, it will be seen that iodine ions retard the reaction, and the slight lowering of the velocity coefficients as the reaction proceeds is due to the continued increase in the concentration of iodine ions, which are products of the reaction.

One peculiar point will be noticed, namely, that if there is a definite concentration of potassium iodide, the velocity coefficient does not depend on the concentration of iodine, but if we start with a definite concentration of iodine and increase the concentration of potassium iodide, the velocity coefficient falls off. This effect cannot be explained from the mass action equilibrium

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 $KI + I_2 \rightleftharpoons KI_3$. In Table I we have 1.27 grams of iodine and 5.4132 grams of potassium iodide and k_1 at $25^\circ = 0.00196$; and in Table V we have 0.635 gram of iodine and 2.7066 grams of potassium iodide and k_1 at $25^\circ = 0.00378$. The concentrations of sodium formate in these two cases are equal, and according to the mass action equilibrium the velocity coefficient should be the same, since the ratio of the concentrations of potassium iodide and iodine is the same in the two cases. This point has been thoroughly studied in the oxidation of sodium formate by mercuric chloride in the presence of several chlorides.

In order to determine the temperature coefficient of the oxidation of sodium formate by iodine, measurements were made at different temperatures. Typical examples of the results obtained are recorded in the following Tables.

TABLE VIII.

3.4004 Grams of sodium formate, 1.27 grams of iodine, and 5.4132 grams of potassium iodide. Volume = 150 c.c.

At 50°.

<i>t</i> .	a - x.	k_1 .
0	98.7	
4	57.3	0.0590
8	$33 \cdot 4$	0.0588
12	19.5	0.0586
16	11.4	0.0585

Mean..... 0.0587

Table I gives k_1 at $25^\circ = 0.00196$; therefore k_{t+10}/k_t between 25° and $50^\circ = 3.89$.

TABLE IX.

0.6801 Gram of sodium formate, 1.27 grams of iodine, and 5.4132 grams of potassium iodide. Volume = 150 c.c.

At 50°.

t.	a-x.	k_1 .
0	98.7	
5	86.35	0.0116
10	75.7	0.0115
18	62.05	0.0112
25	51.8	0.0112
35	40.7	0.0110
	1944 - C.	·
	Mean	0.0113

Table III gives k_1 at $25^\circ = 0.000390$; therefore k_{t+10}/k_t between 25° and $50^\circ = 3.88$.

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TABLE X.

6.8008 Grams of sodium formate, 0.635 gram of iodine, and 2.7066 grams of potassium iodide. Volume=150 c.c.

At 35°.

t.	a-x.	k_1 .
0	39.5	
4	29.3	0.0325
10	19.0	0.0318
15	13.55	0.0310
20	10.05	0.0298

Mean..... 0.0313

Table IV gives k_1 at 25°=0.00781; therefore $k_{35}/k_{25}=4.01$.

From the foregoing results, it is seen that the temperature coefficient of the oxidation of sodium formate by iodine is 4.01 between 25° and 35° and 3.89 between 25° and 50° .

It has already been observed that potassium iodide, or rather iodine ions, act as a negative catalyst in this reaction. In order to determine if there is any change in the temperature coefficient when the reaction is greatly retarded by potassium iodide, measurements were made at different temperatures with various concentrations of potassium iodide. The results obtained are as follows:

1.7002 grams of sodium	$\begin{cases} \text{Grams of potass-}\\ \text{ium iodide} & \dots \\ k_1 \text{ at } 25^\circ & \dots \\ \text{Temperature} \\ \text{coefficient} & \dots \\ \end{cases}$	1.6952	2·1708	9·9086
formate and 0.3354		0.00297	0·000647	0·000470
gram of iodine.		4.01	4·19	4·13
1.7002 grams of sodium formate and 0.3354 - gram of iodine.	$\begin{cases} \text{Grams of potass-}\\ \text{ium iodide} & \dots \\ k_1 \text{ at } 25^\circ & \dots \\ \text{Temperature}\\ \text{coefficient} & \dots \end{cases}$	15·3843 0·000320 4·11	$31.8110 \\ 0.000173 \\ 4.02$	

Hence, even in strongly catalysed reactions, the temperature coefficients are practically the same as those in the feebly catalysed ones.

A few more experiments were made with different concentrations of iodine and potassium iodide, and the experimental results are summarised in the following Tables.

TABLE XI.

1.7002 Grams of sodium formate, 0.1677 gram of iodine. Volume=150 c.c.

Potassium			
iodide.	Mean k_1	Mean k_1	
Grams.	at 25°.	at 35° .	k_{t+10}/k_t .
0.8476	0.00556	0.0229	4.10
9.0610	0.000520	0.00211	4.06
$29 \cdot 8732$	0.000205	0.000833	4.06
78.2492	0.000112	0.000413	3.69

TABLE XII.

0.6801 Gram of sodium formate, 0.1677 gram of iodine. Volume = 150 c.c.

Potassium			
iodide.	Mean k_1	Mean k_1	
Grams.	at 25°.	at 50°.	k_{t+10}/k_t .
0.8476	0.00212	0.0654	3.95
20.1980	0.000111	0.00342	3.93
$29 \cdot 8732$	0.0000804	0.00242	3.90
49.2236	0.0000573	0.00152	3.71

In the results last recorded in this, as well as in the foregoing Table, the concentration of potassium iodide was very great; complexities due to changes of viscosity might have arisen and have caused the temperature coefficients to be lower than the other values in the same series. In this case, we find that the temperature coefficient of the reaction does not change in the presence of potassium iodide.

The effect of manganese sulphate was also studied, and the following is a summary of the results obtained:

Grams of manganese sulphate. Value of k_1 at 25°	$\begin{array}{c} 0\\ 0{\cdot}00751\end{array}$	$0.0524 \\ 0.00749$	$0.1048 \\ 0.00735$	$1.8882 \\ 0.00634$
Grams of manganese sulphate Value of k_1 at 25°	$6.294 \\ 0.00478$	$12 \cdot 588 \\ 0 \cdot 00376$	$18.882 \\ 0.00286$	$37.764 \\ 0.00151$

Evidently the velocity coefficient falls off as the concentration of manganese salt is increased.

Sodium Formate and Mercuric Chloride.

It is well known that formic acid and formates can be oxidised by mercuric chloride. The mechanism of the reduction of mercuric chloride by formic acid and formates has been investigated by Portes and Ruyssen (Compt. rend., 1876, **82**, 1504), Scala (Gazzetta, 1890, **20**, 393), Lieben (Monatsh., 1893, **14**, 750), etc.

Recently Findlay and Davies (T., 1913, 103, 1554) and Linhart (J. Amer. Chem. Soc., 1915, 37, 70) have also studied the problem. From the ordinary method of chemical dynamics they have found that the velocity coefficients follow the bimolecular law.

In order to determine the temperature coefficient and the effect of catalysts on this reaction the following experiments were made.

Since ordinary sodium formate contains a little sodium carbonate, a solution of the salt was carefully neutralised with pure formic acid, evaporated and crystallised. As a rule, the salt was twice crystallised from water and dried centrifugally. A solution was prepared and was standardised by estimating the formic acid with potassium permanganate, and this estimation was checked by evaporating a measured volume of the solution in a platinum crucible, heating the residue with sulphuric acid, and weighing the sodium sulphate formed. The other salts used were generally recrystallised twice. From time to time measured volumes were withdrawn by means of a pipette fitted with a plug of cotton wool, to keep back mercurous chloride, and run into a known volume of potassium iodide; the excess of potassium iodide was then titrated against standard mercuric chloride. It was seen from preliminary work that this method of estimation was quite accurate.

The equation representing the chemical change is the following: $2HgCl_2 + H \cdot CO_2Na = 2HgCl + NaCl + HCl.$

The hydrogen ions formed in the reaction greatly retard the change. In order to avoid this difficulty, 2.11 grams of sodium acetate were added to the reacting mixtures.

The velocity of the reaction may be represented by an equation of the form $-dc_1/dt = kc_1^m c_2^n$, where c_1 and c_2 represent concentrations of mercuric chloride and formate respectively.

Determination of m.—In the following series of experiments, the sodium formate used was in large excess, and hence the concentration may be taken as practically constant during the course of the reaction. Hence the velocity equation takes the following form: $-dc_1/dt = (kc_2^n)c_1^m = k_1c_1^m$, where $k_1 = kc_2^n$. The order of the reaction is therefore the same as m.

TABLE I.

18:3426 Grams of sodium formate, M/15-mercuric chloride. Volume=150 c.c. (where M = molar).

At 25°.

		k_1 (uni-
t.	a - x.	molecular).
0	16.65	
48	12.7	0.00245
75	11-1	0.00235
111	9.5	0.00220
160	7.8	0.00207
	Mean	0.00227

TABLE II.

14.0362 Grams of sodium formate, M/15-mercuric chloride. Volume = 150 c.c. At 25°.

		_
<i>t</i> .	a-x.	k_1 .
0	16.65	
70	12.5	0.00178
125	10.2	0.00170
168	8.8	0.00165
216	7.5	0.00160

Mean..... 0.00168

TABLE III.

At 40°.

t.	a-x.	k_1 .
0	16.65	
8.5	12.4	0.0150
14.0	10.6	0.0140
20.0	9.15	0.0130
25.0	8.1	0.0125
	Mean	0.0136

TABLE IV.

9.1713 Grams of sodium formate, M/15-mercuric chloride. Volume = 150 c.c.

At 25°.

t.	a-x.	k_1 .
0	16.65	
105	12.45	0.00120
165	10.75	0.00115
250	8.95	0.00108
310	7.85	0.00105
	Mean	0.00112

TABLE V.

At 40°.

t.	a - x.	k_1 .
0	16.65	
12.0	12.75	0.00965
22.0	10.5	0.00910
31.3	8.85	0.00877
37.5	$7 \cdot 9$	0.00864
	Mean	0.00904

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TABLE VI.

7.0181 Grams of sodium formate, M/15-mercuric chloride. Volume=150 c.c. At 25°.

t.	a-x.	k_1 .
0	13.34	
61	11.8	0.00087
150	9.9	0·00086
255	8.15	0·00084
550	4 ·9	0.00079

Mean..... 0.00084

TABLE VII.

At 40°.

t.	a-x.	k_1 .
0	13.34	_
14	10.5	0.00743
28	8.6	0.00681
35	7.8	0.00666
56	6.0	0.00620
	M ean	0.00677

From the foregoing Tables it will be seen that, in spite of a slight tendency to fall off, the values of k calculated for m=1 exhibit such a degree of constancy that the equation indicating a unimolecular reaction may fairly be regarded as the appropriate one.

Determination of n.—Supposing that k_1' and k_1'' are the values of k_1 (in the equation $k_1 = kc^n$) obtained in two experiments, in each of which the initial concentration of mercuric chloride is the same, whilst the concentrations of sodium formate are different, say, c_2' and c_2'' , the following equations are obtained: $k_1' = kc_2'^n$, $k_2'' = kc_2''^n$, whence $n = \log \frac{k_1'}{k_{*}''} \log \frac{c_2'}{c_{*}''}$.

On comparing the results recorded in the foregoing tables, the following summary is obtained :---

	(1).	(2).	(3).	(4).
Grams of formate	18.3426	14.0362	9.1713	7.0181
$k_1 \text{ at } 25^{\circ}$	0.00227	0.00168	0.00112	0.00084

By combining these results, the actual values of n obtained are 1.12, 1.02, 1.03, 0.95, 1.0, and 1.08. It is seen that n approaches very closely to the value 1. Hence the oxidation of sodium formate by mercuric chloride is unimolecular with respect to both the reacting substances, and consequently the whole reaction is

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bimolecular. The equation representing the chemical change shows it to be termolecular, and this makes it probable that the reaction takes place in stages.

In order to study the effect of change in the concentration of mercuric chloride, further experiments were made at 25°, the results of which are summarised as follows:

With 7.0181	grams of formate.	sodium	With 9.1713 g for	rams of mate.	sodium
Concentration of $HgCl_2$ k_1 at 25°	M/15 0.00084	$M/30 \\ 0.00087$	Concentration of $\operatorname{HgCl}_2 \dots k_1$ at 25°	$M/15 \ 0.00112$	M/30 0.00116

Hence the velocity coefficients increase very slightly with the decrease in the concentration of mercuric chloride.

Temperature Coefficient of the Reaction.—From Tables II and III we get k_1 at $25^\circ = 0.00168$ and k_1 at $40^\circ = 0.0136$. Hence, applying van't Hoff's equation, we obtain $k_{t+10}/k_t = 4.03$. Similarly, from Tables IV and V and from VI and VII the temperature coefficient obtained is 4.02. It is rather striking that the temperature coefficient of the oxidation of sodium formate by iodine has practically the same value, namely, 4.01.

In order to determine the temperature coefficient between 40° and 50° , the following measurements were made:

TABLE VIII.

3.3805 Grams of sodium formate and M/30-mercuric chloride. Volume=150 c.c.

	At 40°.			At 50°.	
t.	a-x.	k_1 .	t.	a-x.	k_1 .
0	8.32		0	8.32	
42	6.3	0.00288	10	6.55	0.0104
90	4.7	0.00276	25	4.65	0.0101
139	3.5	0.00270	39	3.45	0.0098
	Mean	0.000278	м	ean	0.0101
		Therefore k_{50} ,	$k_{40^{\circ}} = 3.63.$		

Applying the Arrhenius formula, we get A = 5635 from measurements at 25° and 40°, using this value of A for the measurements at 40° and 50° we get $k_{50}^{\circ}/k_{40}^{\circ} = 3.61$, practically the same result as found experimentally.

The effect of manganese sulphate on the oxidation of sodium formate by mercuric chloride was studied, and the results obtained are summarised below:

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TABLE IX.

9.1713 Grams of sodium formate and M/15-mercuric chloride. Volume=150 c.c.

Manganese sulphate. Grams.	$\begin{array}{c} \text{Mean} \ k_1 \\ \text{at} \ 25^\circ. \end{array}$	$\begin{array}{c} \text{Mean } k_1 \\ \text{at 40°.} \end{array}$	k_{t+10}/k_{t} .
0	0.00112	0.00903	4.02
0.0262	0.00111	0.00897	4.03
0.0524	0.00110	0.00889	4.03
1.5735	0.00098	0.00792	4.03
3.147	0.00089	0.00718	4.02
4.7205	0.00085	0.00682	4.01
6.294	0.00081	0.00643	4.0
9.441	0.00070	0.00560	4.0

Thus it appears that the greater the concentration of manganese sulphate the greater is the retardation, and the temperature coefficient in the presence of the negative catalyst is practically unchanged.

From the foregoing Tables it will be seen that, even in the presence of sodium acetate, the velocity coefficient falls off as the reaction proceeds. It was suspected that it might be due to the increase in the concentration of chloride ions. Linhart (*loc. cit.*) observed that sodium chloride retards the reaction. In order to establish this further, measurements were carried out in the presence of chlorides of several metals. Two series of measurements with zinc chloride at 25° are recorded in full in the following Tables, and these show clearly that in presence of an excess of chloride the unimolecular velocity coefficient remains more constant than that obtained when no chloride is present.

9.1713 grams of sodium formate and M/15-mercuric chloride were used in each case, and the volume of the mixture was 150 c.c.:

TABLE X.

Wit	h 1.096N-zinc	chloride.	With	0.73N-zine e	hloride.
t.	a - x.	k_1 .	t.	a - x.	k_1 .
0	16.65	<u> </u>	0	16.65	
1465	13.1	0.000071	860	13.1	0.000121
2820	10.55	0.000070	1340	11.5	0.000120
3960	8.8	0.000070	2345	8.65	0.000121
4945	7.5	0.000070	3835	$5 \cdot 8$	0.000119
	Mean	0.000070	M	əan	0.000120

Further experiments were made with zinc chloride as catalyst at 25° and 40° and the results obtained are summarised below:

Concentration of ZnCl_2 k_1 at 25° Temperature coefficient.	$0 \\ 0.00112 \\ 4.02$	$0.364 \\ 0.000276 \\ 4.16$	$0.730 \\ 0.000120 \\ 4.32$	$1.096 \\ 0.000070 \\ 4.46$
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It appears from the foregoing summary that zinc chloride produces a marked retardation in the reaction, and the greater the concentration of zinc chloride the greater is the retardation and the greater the value of the temperature coefficient.

The effects of calcium, strontium, and sodium chlorides were investigated. Instead of detailed results, the following summary is given:

TABLE XI.

9.1713 Grams of sodium formate and M/15-mercuric chloride. Volume=150 c.c.:

Concentration	Mean k_1	Mean k_1	
of chloride.	at 25°.	at 40°.	k_{t+10}/k_t
0	0.00112	0.00904	4.02
0.4016 N-CaCl ₂	0.000292	0.00246	4.13
0.8032 ,,	0.000142	0.00123	4.22
1.205 ,,	0.000080	0.000732	4.38
1.6066 ,,	0.000058	0.000552	4.49
3.2134 ,,	0.000020	0.000195	4.58
$0.74 N-\mathrm{SrCl}_2$	0.000164	0.00141	$4 \cdot 20$
1.48 ,,	0.000076	0.000698	4.39
0·4914 N-NaCl	0.000296	0.00246	4.09
0.7234 ,,	0.000230	0.00194	4.15
0.9826 ,,	0.000163	0.00138	$4 \cdot 16$
1.085 ,,	0.000154	0.00133	4.21
1.4466 ,,	0.000114	0.00104	4.36

Summary of results obtained with manganese chloride:

Concentration of MnCl.	0	0.1722	0.4306	0.8612	1.7226
$k_1 \text{ at } 25^{\circ} \dots$	0.00112	0.000486	0.000207	0.000081	0.000025
Temperature coefficient.	4.02	4.06	$4 \cdot 20$	$4 \cdot 42$	4.54

All these chlorides produce a marked retarding effect; with equivalent concentrations the maximum effect is observed with zinc and manganese chlorides; both zinc and manganese ions have been found to act as retarders in the oxidation of sodium formate by mercuric chloride. The temperature coefficient is always greater the greater the retardation.

The effect of the change in the concentration of mercuric chloride was also investigated. Calcium, strontium, and sodium chlorides were used as retarders, and the concentrations of mercuric chloride were varied from M/7.5 to M/50. From the experimental results it was seen that with a given concentration of the chloride the velocity coefficient was independent of the concentration of mercuric chloride. If, however, the effect of the chloride be simply to form a complex with mercuric chloride $HgCl_2 + RCl \rightarrow RHgCl_3$ (compare Le Blanc and Noyes, *loc. cit.*), the velocity coefficient would naturally depend on the concentrations of mercuric chloride. It was also seen that the greater the concentration of the catalyst, the greater the retardation and the greater the value of the temperature coefficient. The retarding effect of chlorides on this reaction is provisionally considered to be catalytic.

It has already been said that hydrogen ions retard the oxidation of sodium formate by mercuric chloride; hence it seems probable that only formate ions are active in effecting the reduction. In order to confirm this point, a few measurements were made with pure formic acid. The experimental procedure is exactly the same as with formates; the presence of free formic acid does not interfere with the estimation of mercuric chloride by potassium iodide.

TABLE I.

0.678 N-formic acid and M/30-mercuric chloride.

At 25°.

t (time in		k_1 (uni-
minutes).	a - x.	molecular).
0	8.3	
4500	7.25	0.0000131
12540	6.2	0.0000101
20890	5.65	0.0000080
		·

Mean..... 0.0000104

TABLE II.

At 40°.

t.	a-x.	k_1 .
0	8.3	<u> </u>
670	7.0	0.000110
1500	6.25	0.000082
2980	5.5	0.000060

Mean...... 0.0000840Therefore $k_{t+10}/k_t = 4.02$.

The unimolecular velocity coefficient falls off owing to the accumulation of hydrogen chloride, which suppresses the ionisation of formic acid and at the same time forms complexes with mercuric chloride.

In order to obtain comparable results, readings were taken for times of almost equal changes in different experiments (compare Le Blanc and Noyes, *Zeitsch. physikal. Chem.*, 1890, **6**, 389). The chemical equation for the change is:

 $2 HgCl_2 + H \cdot CO_2 H = 2 HCl + CO_2 + 2 HgCl.$

The following is a summary of the results with formic acid and mercuric chloride:

Concentration of formic acid	0.678	1.356	2.032	4.064
$k_1 \text{ at } 25^{\circ} \dots$	0.0000104	0.0000155	0.0000167	0.0000199
Temperature coefficient	4.02	4.02	3.99	4.01

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It will be seen that the velocity of the reduction of mercuric chloride by formic acid is much smaller than the velocity of reduction by sodium formate of the same concentration. Moreover, the velocity coefficient does not increase proportionally with the increase in the concentration of formic acid. The electrical conductivity and freezing-point measurements of Novák (Phil. Mag., 1897. [v]. 46, 9) show that, by doubling the concentration of formic acid, a small increment of formate ions is produced in the solutions, and this is corroborated by kinetic measurements, which show that by doubling the concentration of formic acid we get only a small increment in the value of the velocity coefficient, and kinetic measurements also prove that only formate ions are active in the reduction; the undissociated formic acid is inactive so far as the reduction of mercuric chloride is concerned. Moreover, the temperature coefficient of this reaction is 4.02, which is exactly the same as that obtained in the reduction by formates; this shows that the processes of reduction of mercuric chloride by sodium formate and formic acid are similar in nature. On the other hand, it has been proved before that the oxidation of formic acid by chromic acid is a quadrimolecular reaction, that only undissociated formic acid is active in this reaction, and that the temperature coefficient has the value 2.07. Evidently, even with the same reducing agent, the nature of the chemical change is totally different with different oxidising agents.

Silver Nitrate and Sodium Formate.

It is well known that silver for very accurate work is usually prepared by the reduction of silver nitrate by formates, and this reaction is largely utilised in analytical chemistry. It seemed desirable to investigate the kinetics of the reaction. When silver nitrate is added to a moderately concentrated solution of sodium formate at about 25°, there is produced at first a very slight opalescence due to the formation of silver formate; then after a few seconds the silver formate begins to decompose with the separation of a black voluminous mass of metallic silver. Then, in consequence of the presence of electrolytes, the volume of the reduced silver becomes less and less, and finally a small quantity of more compact grey metallic silver is obtained.

The reduction, slow as it is, at 25° is quite measurable, even at that temperature.

Standard solutions of purified silver nitrate and sodium formate were prepared. The experimental procedure is similar to that in the oxidation of formates by mercuric chloride. After given intervals of time, measured volumes of the mixture were removed by means of a pipette fitted with a small filtering plug and run into an excess of a standard solution of sodium chloride. The excess of chloride was then titrated by means of a standard silver nitrate solution, using potassium chromate or potassium arsenate as an indicator. In order to diminish the concentration of hydrogen ions, 2.11 grams of sodium acetate were used in each observation.

The reaction velocity may be represented by an equation of the form $-dc_1/dt = kc_1^{m}c_2^{n}$ where c_1 and c_2 represent the concentrations of silver nitrate and sodium formate respectively, and m and n the number of these molecules taking part in the reaction.

Determination of m.—In the following series of experiments, the concentration of sodium formate was much greater than that of silver nitrate, and as this does not appreciably alter during the course of the reaction, the velocity equation takes the following form:

$$-dc_1/dt = (kc_2^n)c_1^m = k_2c_1^m,$$

where $k_2 = kc_2^n$. The order of the reaction is the same as m.

In the following Tables the amounts in c.c. of unchanged silver nitrate are recorded:

TABLE I.

3.4205 Grams of sodium formate and N/15-silver nitrate. Volume=150 c.c.

At 25°.

		k_2	k_1
Time in	Unchanged	(bimolecular	(unimolecular
minutes.	silver nitrate.	m=2).	m = 1).
0	13.3		_
162	11.2	0.0000869	0.000461
449	8.75	0.0000870	0.000405
800	6.9	0.0000871	0.000356
1355	$5 \cdot 2$	0.0000866	0.000301
	Mean	0.0000869	

TABLE II.

9.1713 Grams of sodium formate and N/15-silver nitrate. Volume=150 c.c.

Δŧ.	25	0
110	40	•

		ĸ,
t.	a-x.	(bimolecular)
0	13.3	
179	8.9	0.000208
365	6.6	0.000209
766	4.25	0.000208
1436	2.65	0.000210
	Mean	0.000209

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TABLE III.

At 40°.

t.	a-x.	k_2 .
0	13.3	
70	7.15	0.000916
182	4.15	0.000911
303	2.85	0.000910
528	1.8	0.000910
	36	0.000010
	Mean	0.000912

TABLE IV.

At 50°.

t.	a - x.	k_2 .
0	13.3	
19	8.5	0.00224
38	6.2	0.00227
64	4.55	0.00226
177	2-1	0.00227
	Mean	0.00226

TABLE V.

16.508 Grams of sodium formate and N/15-silver nitrate. Volume=150 c.c.

At 25°.

t.	a-x.	k_2 .
0	13.3	
172	$7 \cdot 2$	0.000370
327	$5 \cdot 1$	0.000370
517	3.75	0.000370
1484	1.6	0.000370
	M ean	0.000370

TABLE VI.

At 40°.

t.	a-x.	k_2 .
0	13.3	
32	7.9	0.00161
82	4.8	0.00162
129	3.55	0.00161
	Mean	0.00161

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TABLE VII.

At 50°.

<i>t</i> .	a-x.	k_2 .
0	13.3	
10.5	8.5	0.00404
18.5	6.65	0.00406
60.5	3.1	0.00409
	M ean	0.00406

The values of k_2 calculated for m=2 show such a degree of constancy that the equation indicating a bimolecular reaction may fairly be regarded as the appropriate one. The oxidation is evidently bimolecular with respect to silver nitrate.

Determination of n.—Supposing that k_1' and k_2'' are the values of k_2 obtained in two experiments, in each of which the initial concentration of silver nitrate is the same, whilst the concentrations of sodium formate are different, say c_2' and c_2'' , the following equations are obtained: $k_2' = kc_2'^n$, $k_2'' = kc_2''^n$, whence

$$n = \log \frac{k_2'}{k_2''} / \log \frac{c_2'}{c_2''}.$$

On comparing the foregoing measurements recorded at 25°, the following summary is obtained:

	(1).	(2).	(3).
Grams of formate	16.508	9.1713	3.4205
$k_2 \text{ at } 25^{\circ}$	0.000370	0.000209	0.0000868

By combining these results, the values of n actually obtained are 1.09, 0.96, and 0.90. It is seen n approaches closely to the value 1, and consequently 1 molecule of sodium formate takes part in the reaction. The whole reaction is, therefore, termolecular, bimolecular with respect to silver nitrate, and unimolecular with regard to sodium formate (compare Noyes and Cottle, Zeitsch. physikal. Chem., 1898, **27**, 579).

In order to study the change in the concentration of silver nitrate on the velocity coefficient of this reaction, further measurements were made at 25°, and the results obtained are summarised below:

With 9.1713 grams of sodium formate:

Concentration of AgNO ₈	N/15	N/30	N/50
k ₂ at 25°	0.000209	0.000212	0.000210

With 16.508 grams of sodium formate:

Concentration of AgNO ₃	N/15	N/30
k_2 at 25°	0.000370	0.000372

With 3 4205 grams of sodium formate:

Concentration of AgNO ₃	N/15	N/30
k_2 at 25°	0.0000869	0.0000870

Evidently change in the concentration of silver nitrate has practically no influence on the velocity coefficients, hence there is no disturbing factor, and the reaction is truly termolecular.

The chemical equation for this reaction is:

 $2 \operatorname{AgNO}_3 + \operatorname{H} \cdot \operatorname{CO}_2 \operatorname{Na} = \operatorname{HNO}_3 + \operatorname{NaNO}_3 + \operatorname{CO}_2 + 2 \operatorname{Ag}.$

Hence the reaction is simple and does not take place in stages.

Temperature Coefficient.—From Tables II, III, and IV we get k_2 at $25^\circ = 0.000209$, k_2 at $40^\circ = 0.000912$, and k_2 at $50^\circ = 0.00226$. Hence by applying van't Hoff's formula we get k_{t+10}/k_t between 25° and $40^\circ = 2.67$, and between 40° and $50^\circ = 2.48$.

If the Arrhenius formula is used, the following results are obtained:

t.	k_{2} (obs.).	k_2 (calc.).
25°	0.000209	(0.000209)
40°	0.000912	(0.000912)
50°	0.00226	0.00226
	A = 3977.	

It has been previously shown that the temperature coefficient of the oxidation of sodium formate by iodine and mercuric chloride has the value 4.02 between 25° and 40° , and both these reactions are bimolecular. Although the oxidation of sodium formate by silver nitrate is a much slower reaction than the other two, the temperature coefficient is much lower than those in the other cases. Evidently there seems to be a connexion between the order of a reaction and its temperature coefficient. From this investigation it will be clear that under similar conditions iodine is a better oxidising agent than mercuric chloride and the latter is a much better oxidising agent than silver nitrate. Evidently from kinetic measurements, under exactly similar conditions, we can compare the relative oxidising or reducing property of substances quite accurately.

The effect of a manganese salt was studied.

The results obtained with manganese sulphate as catalyst are summarised below:

9.1713 Grams of sodium formate and N/15-silver nitrate. Volume = 150 c.c.

sulphate. Grams.	$\begin{array}{c} \operatorname{Mean} k_2 \\ \operatorname{at} 25^\circ. \end{array}$	$\begin{array}{c} \operatorname{Mean} k_2 \\ \operatorname{at} 40^\circ. \end{array}$	Temperature coefficient.
0	0.000209	0.000912	2.67
0.0524	0.000207	0.000905	2.67
1.5735	0.000187	0.000811	2.66
3.147	0.000170	0.000740	2.66
6.294	0.000142	0.000621	2.67
12.588	0.000109	0.000475	2.66

From the above figures it appears that manganese sulphate is a negative catalyst in the oxidation of sodium formate by silver nitrate. The greater the concentration of the catalyst, the greater is the retardation. This reaction, like the oxidation of sodium formate by mercuric chloride, is not so sensitive to the influence of traces of manganese sulphate as the oxidation of formic acid by chromic acid previously studied. Moreover, the temperature coefficient is the same as that obtained without any manganese sulphate.

Mechanism of Chemical Change and Temperature-Coefficient.

It is well known that temperature has a marked influence on the velocity of reactions, the average value of the temperaturecoefficient being about 2.5 for a rise of 10° in the case of nonactinic chemical changes. This exponential increase of velocity with temperature cannot be explained from the mere increase in kinetic movement, for this should mean an increase of only about 2 per cent. in the velocity of the reaction for the same change of temperature. It is clear, therefore, that the temperature effect must be due to some influence connected with the internal structure of the molecules taking part in the reaction.

The phenomena of ordinary positive catalysis as well as photochemical catalysis in homogeneous medium have made us familiar with the acceleration of reactions at constant temperature, and this must similarly be due to some effect connected with the structure of the molecules.

It seems, therefore, probable that the effects of increase of temperature, of light, and of chemical catalysts in a reaction are intimately connected and are possibly identical in nature.

As was first suggested by Arrhenius (Zeitsch. physikal. Chem., 1889, 4, 226), the effect of temperature has been ascribed to the existence of an equilibrium between so-called "active" and "inactive" molecules, such equilibrium being sensitive to changes of

temperature; and hence a rise of temperature by bringing into existence more "active" molecules causes a reaction velocity very much in excess of what one would expect on a merely kinetic view.

Arrhenius has even deduced an expression $d \log k/dT = A/T^2$, showing the effect of temperature in terms of a quantity A, which on this view is taken to be half the energy change involved in the transformation of one molecule of "inactive" to "active."

If such "active" and "inactive" molecules exist, it appears reasonable to expect that a catalyst or light simply acts in shifting this equilibrium. Plainly if sufficient catalyst were added to change a relatively large amount of "inactive" to "active" molecules or *vice versa*, it would follow that, when the catalyst is present in large quantities, the temperature coefficient should be smaller (in the case of positive catalysis) and greater (in the case of negative catalysis) than that observed when the reaction is not catalysed or only feebly so. For when much catalyst is present, the transformation from "inactive" to "active" in the case of positive catalysis would have already taken place, and therefore temperature should have less additional accelerating effect; the reverse would be the case in negative catalysis. This hypothesis can be tested by the experiments with chemical catalysts already recorded in this paper.

In order to apply the hypothesis to photochemical catalysis, the following investigations were carried out. Goldberg (Zeitsch. physikal. Chem., 1902, 41, 1; Zeitsch. wiss. Photochem., 1906, 4, 61), who studied the oxidation of quinine sulphate by chromic acid in light, found the temperature coefficient of the reaction to be 1.04 for a 10° rise in temperature. The temperature coefficient of this reaction in the dark has been determined by the author as described below.

In order to exclude light, "resistance" glass bottles were thoroughly covered with a thick coating of "club black enamel." This enamel can withstand hot water fairly well, and light is completely excluded by a thick coating. The chromic acid, which remained unchanged, was estimated by iodometric measurement with standard thiosulphate.

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Quinine and Chromic Acid.

TABLE I

1.322 Grams of quinine sulphate, N/85-chromic acid, and 30N/17-sulphuric acid. Volume=85 c.c.

At 25°.

		k_1 (uni-
t.	a-x.	molecular).
0	8.15	
450	7.0	0.000150
1420	4.95	0.000152
3210	$2 \cdot 6$	0.000154
		···

Mean..... 0.000152

TABLE II.

At 60°.

t.	a-x.	k_1 .
0	8.12	
101	5.9	0.00137
187	4.5	0.00137
290	$\overline{3} \cdot \overline{2}$	0.00139

Mean..... 0.00138

Therefore temperature coefficient between 25° and 60° = $k_{t+10}/k_t = 1.88$.

TABLE III.

1.322 Grams of quinine sulphate, N/85-chromic acid, and 60N/17-sulphuric acid. Volume=85 c.c.

At 25°.

t.	a-x.	k_1 .
0	8.15	
258	6.9	0.000281
540	5.75	0.000280
1590	$2 \cdot 9$	0.000282
	Mean	0.000281
	TABLE IV.	
	At 60°.	
t.	a-x.	k_1 .
0	8.12	
43.5	6.3	0.00254
67	5.5	0.00252
100	4.5	0.00255
150	3.37	0.00254
	M ean	0.00254

Therefore k_{t+10}/k_t between 25° and 60° = 1.87.

Sulphuric acid only accelerates the reaction and was used by Goldberg in his work. The reaction, carried on in the dark, has a higher value (1.87) for its temperature coefficient than that in the light (1.04) under similar conditions. Thus the acceleration caused by the positive catalyst (light) produces a marked lowering of the temperature coefficient.

Iodine and Potassium Oxalate.

In a former paper (Dhar, Proc. K. Akad. Wetensch. Amsterdam, 1916, 18, 1097) it was found that the oxidation of oxalates by iodine was very sensitive to light; light acted here as a strong positive catalyst. This reaction was investigated in diffused daylight and in the dark. The reaction in the case of potassium oxalate may be represented by the equation

 $K_2C_2O_4 + I_2 \longrightarrow 2KI + 2CO_2.$

As in the case of the formate oxidation, sublimed iodine was used and the potassium oxalate was purified by several recrystallisations and carefully dried centrifugally. The solution of oxalate was standardised by precipitating a known volume as calcium oxalate, igniting in a platinum crucible, and weighing as lime.

From time to time the unchanged iodine was estimated by means of standard sodium thiosulphate.

The velocity of the reaction may be represented by an equation of the form $-dc_1/dt = kc_1^m c_2^n$, where c_1 and c_2 represent concentrations of iodine and oxalate respectively.

Determination of m.—In the following series of experiments the oxalate used was in large excess, and hence the concentration might be supposed to be practically constant during the course of the reaction; hence the velocity equation takes the following form:

$$-dc_1/dt = (kc_2^n)c_1^m = k_1c_1^m,$$

where $k_1 = kc_2^n$. The order of the reaction is the same as m.

Measurements in the Dark at 50°.

TABLE V.

18.7080 Grams of potassium oxalate, 0.1677 gram of iodine, and 0.8476 gram of potassium iodide. Volume=150 c.c.

		k_1 (uni-
t.	a-x.	molecular).
0	14.37	_
90	9.24	0.00213
155	6.6	0.00218
220	4.7	0.00220
280	3.4	0.00223
	M ean	0.00218

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TABLE VI.

9.354 Grams of potassium oxalate, 0.1677 gram of iodine, and 0.8476 gram of potassium iodide. Volume = 150 c.c.

<i>t</i> .	a - x.	k_1 .
0	14.37	
100	11.5	0.000967
260	8.0	0.000978
485	4.8	0.000981
	Mean	0.000975

TABLE VII.

4.6770 Grams of potassium oxalate, 0.1677 gram of iodine, and 0.8476 gram of potassium iodide. Volume=150 c.c.

t.	a-x.	k_1 .
0	14.37	
245	11.2	0.000442
500	8.5	0.000456
725	$6 \cdot 6$	0.000466
	Mean	0.000455

From the foreging Tables, it will be seen that the values of k calculated for m=1 exhibit such a degree of constancy that the equation indicating a unimolecular reaction may fairly be regarded as the appropriate one.

Determination of n.—Supposing that k'_1 and k''_2 are the values of k_1 (in the equation $k_1 = kc^n$) obtained in two experiments, in each of which the initial concentration of iodine is the same, whilst the concentrations of potassium oxalate are different, say c_2' and c_2'' , the following equations are obtained:

$$k_1' = kc_2'^n, \ k_1'' = kc_2''^n; \ \text{whence} \ n = \log \frac{k_1'}{k_1''} |\log \frac{c_1'}{c_2''}|$$

From the measurements recorded in the foregoing Tables, the following summary of results is obtained:

	(1).	(2).	(3).	$\left(\begin{array}{c} 0.1677 \text{ gram of} \\ \text{ioding and } 0.8476 \end{array}\right)$
Grams of oxalate Value of <i>k</i> at 50°	18·7080 0·00217	9·354 0·000975	$4.677 \\ 0.000455$	gram of potassium iodide.

Combining these results, the values of n actually obtained are 1.1, 1.1, and 1.09.

It is seen that n approaches very closely to the value 1. These results show that the oxidation of potassium oxalate by iodine is unimolecular with respect to both iodine and potassium oxalate, and consequently the whole reaction is bimolecular; this is quite

in accordance with the equation representing the chemical change.

In order to determine the temperature coefficient of the reaction in the dark, measurements were made at different temperatures.

TABLE VIII.

18.7080 Grams of potassium oxalate, 0.1677 gram of iodine, and 0.8476 gram of potassium iodide. Volume = 150 c.c.

		At	2 5°.			
	t.	a - x.		k_1	•	
	0	14.37			_	
	7,015	10.8		0.000	0177	
	12,835	8.4		0.000	0181	
	24,000	4.95		0.000	0193	
		Mear	ı	0.000	0184	
	TABLE IX.		1		TABLE X.	
	At 40°.				At 60°.	
t.	a-x.	k ₁ .		t.	a-x.	k_1 .
0	14.37			0	14.37	
265	11.65	0.000343		14	10.0	0.0113
520	9.35	0.000358		31	6.25	0.0119
1270	4.9	0.000367		47	3.9	0.0121
	Mean	0.000356			Mean	0.0118

Summary of Results.

18.708 grams of potassium oxalate, of **0**∙1677 Temperature 25° 40° 50° 60° gram iodine, and 0.8476 0.00001840.000356 0.00218 0.0118 k_1 gram of potassium iodide

Hence k_{t+10}/k_t between 25° and 40°=7.2, between 40° and 50°= 6.1, and between 50° and 60°=5.4. It is seen that the temperature coefficient of the oxidation of oxalates by iodine in the dark is quite large and is 7.2 between 25° and 40°, and falls off with increase of temperature.

Applying the Arrhenius formula $\log k_1/k_2 = A(T_1 - T_2)/T_1T_2$, the following results are obtained; A = 7989:

Tempera-		
ture.	k (found).	k (calc.).
25°	0.0000184	(0.0000184)
40°	0.000356	(0.000356)
50°	0.00218	0.00219
60°	0.0118	0.0121

The same reaction was studied in diffused daylight. The reaction velocity was greater in diffused daylight than in the dark.

In Diffused Daylight at 50°.

TABLE XIII.

18:7080 Grams of potassium oxalate, 0:254 gram of iodine, and 1:0826 grams of potassium iodide. Volume=150 c.c.

t.	a-x.	k_1 (uni-molecular).
0	19.7	,
65	13.8	0.00238
170	7.75	0.00238
315	$3 \cdot 4$	0.00242
	Mean	0.00239

TABLE XIV.

9.354 Grams of potassium oxalate, 0.254 gram of iodine, and 1.0826 grams of potassium iodide. Volume=150 c.c.

		k_1 (uni-
t.	a-x.	molecular).
0	19.7	
90	15.8	0.00106
210	11.85	0.00105
341	8.85	0.00102
480	6.4	0.00102
	M ean	0.00104

TABLE XV.

4.677 Grams of potassium oxalate, 0.254 gram of iodine, and 1.0826 grams of potassium iodide. Volume = 150 c.c.

t.	a-x.	k_1 .
0	19.7	
120	16.9	0.000555
240	14.6	0.000542
360	12.7	0.000530
480	11.0	0.000527
	Mean	0.000539

Summary of Results.

	(a •)	(1).	(2).	(3).
0.254 gram of lodine and 1.0826 grams of potass- ium iodide	Grams of potass- ium oxalate k_1 at 50°	18·708 0·00239	9·354 0·00104	4·677 0·000539

Combining these results, the values of n actually obtained are 1.2, 1.07, and 0.90. Hence it is seen that n approaches unity. Consequently the reaction is unimolecular with respect to both iodine and oxalate, and the order of the reaction is not altered in diffused light.

In order to determine the temperature coefficient in diffused daylight, measurements were made at 25°.

TABLE XVI.

18.708 grams of potassium oxalate, 0.254 gram of iodine, oxalate, 0.2295 gram of iodine, and 1.0826 grams of potassium iodide. Volume=150 c.c.

t.	a - x.	k_1 .	<i>t</i> .	a - x.	k ₁ .
0	19.7		0	19.66	
360	17.9	0.000114	480	18.9	0.0000356
1440	13.55	0.000113	1440	17.45	0.0000359
2880	9.5	0.000110	11000	8.0	0.0000355
Mea	n	0.000112		Mean	0.0000357

Summary of Results.

 18.7080 grams of potassium oxalate, 0.254 gram of iodine, and 1.0826 grams of potassium iodide 	$\begin{cases} \text{Temperature} \\ \text{Value of } k_1 \end{cases}$	$\substack{\textbf{A.}\\25^{\circ}\\0.000112}$	50° 0∙00239
4.677 grams of potassium oxalate, 0.2295 gram of iodine, and 0.6492 - gram of potassium iodide	$ \begin{cases} \text{Temperature} \\ \text{Value of } k_1 \end{cases} $	B. 25° 0·0000357	50° 0.000741

From A:

Temperature coefficient between 25° and $50^{\circ} = 3.40$. and from B:

 k_{t+10}/k_t between 25° and 50°=3.36.

The temperature coefficient between 25° and 50° of the oxidation of potassium oxalate by iodine in the dark has the value 6.73; whilst in diffused light it is 3.4.

Evidently the acceleration of the oxidation of potassium oxalate by iodine in diffused daylight produces a lowering in the value of the temperature coefficient.

Mercuric Chloride and Potassium Oxalate.

It is well known that a mixture of an oxalate and mercuric chloride has been utilised as an actinometer. Eder (Sitzungsber. K. Akad. wiss. Wien, October, 1879) has made a thorough study of this actinometer and has measured the amount of mercurous

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4.677grams of potassium

TABLE XVII.

and 0.6492 gram of potassium iodide. Volume=150 c.c.

chloride obtained at various temperatures in the presence of light. His results show that the temperature coefficient for a 10° rise between 0° and 80° is 1.19.

In the present investigation the velocity of this reaction at different temperatures in the dark was studied. The reaction being slow, measurements were made at 79.6° and 99.6° with glycerol as the thermostat liquid.

Since preliminary experiments showed that carbon dioxide, which is a product of the chemical reaction, markedly accelerates the change. Both the reacting substances were saturated with carbon dioxide before mixing. As in the case of the oxidation of formates by mercuric chloride, definite volumes of the mixture were withdrawn from time to time by means of a pipette fitted with a plug of cotton-wool, and added to an excess of potassium iodide. The excess of potassium iodide was titrated against a standard solution of mercuric chloride.

> In the Dark. TABLE I.

At 99.6°.

31.430 Grams of potassium oxalate and M/15-mercuric chloride. Volume=150 c.c.

t.	a - x.	k_1 (unimolecular).
0	13.3	
58	9.4	0.00260
140	5.75	0.00260
270	$2 \cdot 6$	0.00262
	Mean	0.00261

TABLE II.

At 99.6°.

15.715 Grams of potassium oxalate and M/15-mercuric chloride. Volume = 150 c.c.

	a-x.	k_1 .
0	13-3	_
142	8.7	0.00130
280	5.75	0.00130
418	3.7	0.00133
	Mean	0.00131

TABLE III.

At 99.6°.

7.8575 Grams of potassium oxalate and M/15-mercuric chloride. Volume=150 c.c.

t.	a - x.	k_1 .
0	13.3	_
343	8.0	0.000643
535	6.0	0.000646
1060	$2 \cdot 7$	0.000653
	Mean	0.000647

TABLE IV.

At 79.6°.

31.430 Grams of potassium oxalate and M/15-mercuric chloride. Volume=150 c.c.

t.	a-x.	k_1 .
0	13.3	
415	8.1	0.00052
610	6.5	0.00051
925	4.3	0.00053
	Mean	$. \frac{1}{0.00052}$

TABLE V.

At 79.6°.

15.765 Grams of potassium oxalate and M/15-mercuric chloride. Volume=150 c.c.

t.	a-x.	k_1 .
0	13.3	
570	2.45	0.00026
1380	5.65	0.00027
1680	4.5	0.00028
	Mean	 0.00027

TABLE VI.

At 79.6°.

7.8575 Grams of potassium oxalate and M/15-mercuric chloride. Volume=150 c.c.

<i>t</i> .	a-x.	k_1 .
0	13.3	
1124	9.5	0.00013
1555	8.35	0.00013
2630	5.7	0.00014
	Mean	0.000133

From the foregoing Tables it will be seen that, in spite of a slight tendency to rise, the values of k calculated for m=1 exhibit such a degree of constancy that the equation indicating a unimolecular reaction may fairly be regarded as the appropriate one.

Determination of n.—Supposing that k_1' and k_1'' are the values of k_1 (in the equation $k_1 = kc^n$) obtained in two experiments, in each of which the initial concentration of mercuric chloride is the same, whilst the concentrations of potassium oxalate are different, say c_2' and c_2'' , the following equations are obtained:

$$k_1' = kc_2'^n, kc_1'' = kc_2'^n; \text{ whence } n = \log \frac{k_1'}{k_1''} \left| \log \frac{c_2'}{c_2''} \right|$$

The measurements recorded in the foregoing Tables may, therefore, be employed in determining the value of n.

On comparing, the following summary of results is obtained :

At 99.6°.

	(1).	(2).	(3).
Grams of oxalate	30.430	15.715	7.8575
Value of k_1	0.00261	0.00131	0.000647

Combining these results, the values of n actually obtained are 1, 1.06, 1.02. It is seen that n approaches very closely to the value 1. Consequently the oxidation of potassium oxalate by mercuric chloride is unimolecular with respect to both the reacting substances, that is, the whole reaction is bimolecular, although the chemical equation shows it to be termolecular:

$$2\mathbf{H}\mathbf{g}\mathbf{C}\mathbf{l}_2 + \mathbf{K}_2\mathbf{C}_2\mathbf{O}_4 = 2\mathbf{H}\mathbf{g}\mathbf{C}\mathbf{l} + 2\mathbf{K}\mathbf{C}\mathbf{l} + 2\mathbf{C}\mathbf{O}_2.$$

The reaction probably takes place in stages.

From Table I we get k_1 at $99.6^\circ = 0.00261$ and from Table IV k_1 at $79.6^\circ = 0.00052$; therefore by van't Hoff's equation we get $k_{t+10}/k_t = 2.24$. Similarly from Tables II and V, also from III and VI, the temperature coefficients obtained are 2.20 and 2.21. Hence it is seen that the temperature coefficient of the oxidation of potassium oxalate by mercuric chloride in the dark is 2.2, whilst in light it is 1.19. Light acting as an accelerator produces a concomitant reduction in the temperature coefficient.

There are a few cases on record where reactions have been investigated both in the light and in the dark.

Brunner and Dluska (Bull. A cad. Sci. Cracow, 1907, 707) have studied the bromination of toluene and found the temperature coefficient in light to be equal to 1.8, whilst in the dark it is 4.5.

Plotnikov (Zeitsch. physikal. Chem., 1907, 58, 64, 214; 1911, 75, 385) also investigated two reactions and found the following values:

Oxidation of Hydrogen Iodide by Oxygen.

		In the light.	In the dark.
Temperature coefficient for 10°	rise	1.4	2.86

Action of Oxygen on Iodoform dissolved in Benzene or Alcohol.

	In the light.	In the dark.
Temperature coefficient for 10° rise	$1 \cdot 42$	2.61

In all these cases light acts as a positive catalyst and markedly accelerates the reactions. Evidently when there is acceleration produced by light we have a concomitant lowering of the temperature coefficient, and the greater the acceleration the greater will be the lowering of the temperature coefficient of the light reaction.

In reactions in which the velocity is greatly accelerated by light we expect the value of the temperature coefficient to be about 1.04 to 1.39; but when light acts as a negative catalyst we should expect an increase in the value of its temperature coefficient.

As a matter of fact, Trautz (*Physikal. Zeitsch.*, 1906, 7, 899) has shown that the oxidation of sodium sulphide and of pyrogallol by oxygen are retarded by violet light, and he has found the temperature coefficients to be 3.5 in the case of sodium sulphide and 2.4 in the case of pyrogallol. These temperature coefficients are much larger than those for photochemical reactions, in which light is an accelerator.

Slator (Zeitsch. physikal. Chem., 1903, 45, 513) investigated the chlorination of benzene in the presence of several chemical catalysts and of light. The reaction velocity in absence of any catalyst is very small. Of the three positive catalysts used in this reaction, iodine chloride, stannic chloride, and ferric chloride, the first was found to be the most effective, then stannic chloride, and lastly ferric chloride. The temperature coefficients in the presence of these catalysts are as follows:

Catalyst	1Cl	$SnCl_4$	FeCl ₈
Temperature coefficient		-	Ū
$=k_{t+10}/k_t$	1.05	1.5	$2 \cdot 5$

Light also accelerates the reaction, and the temperature coefficient in the presence of light is 1.5. It is clear that the greater the acceleration produced by a given catalyst, the smaller is the value of the temperature coefficient; the temperature coefficient of the reaction with the strong positive catalyst, iodine chloride, in the dark is much smaller than that of the reaction carried on in the light without any chemical catalyst. A strongly catalysed reaction in the dark may have a very small temperature coefficient, just like a photochemical reaction. This is in harmony with the hypothesis.

Recent work of Padoa (Atti R. Accad. Lincei, 1916, [v], **25**, ii, 168, 215) has brought further evidence in favour of the hypothesis in question. He has studied the temperature coefficients of the action of monochromatic light on chlorine-hydrogen mixtures, on a photographic plate, and on some phototropic transformations. With the chlorine-hydrogen mixture the following temperature coefficients were obtained:

White light, 1.29; green $(\lambda = 550-530 \ \mu\mu)$, 1.50; blue $(\lambda = 490-470 \ \mu\mu)$, 1.31; violet $(\lambda = 460-40)$, 1.21; ultra-violet $(\lambda = 400-350)$, 1.17.

Thus the value of the temperature coefficient increases with the wave-length of light. The chemical activity of these rays increases with the decrease of the wave-length.

Exactly similar results have been obtained with the photographic plate and the phototropic transformations; the greater the intensity (and hence the acceleration), the smaller is the temperature coefficient.

From a consideration of the experimental verification of this hypothesis in the case of chemical catalysts, it is found that sulphuric acid markedly accelerates the oxidation of formic acid by chromic acid, and in this case the accelerating effect increases more rapidly than the accelerator, and if the concentrations of sulphuric acid are plotted as abscissæ, and the corresponding velocity coefficients as ordinates, an exponential curve is obtained (compare Rosanoff, J. Amer. Chem. Soc., 1913, **35**, 173). According to this hypothesis, the temperature coefficient in the presence of sulphuric acid should be less than that in the absence of the catalyst. As a matter of fact, all the experimental work with sulphuric acid recorded in the foregoing pages supports this deduction. Here only one typical case is cited:

3.0833 N-formic acid and	$\int_{k}^{k} Concentration of H_2SO hot was 25°$	4 0	N/6	N/3	2N/3
N/30-chromic acid	$\begin{cases} \kappa_{t+10}/\kappa_t & \text{between } 25\\ \text{and } 50^\circ \dots \end{pmatrix}$	2.03	1.87	1.86	1.84

Hence we find that the greater the concentration of sulphuric acid, the greater is the fall in the temperature coefficient.

On the other hand, manganese chloride is a negative catalyst in the exidation of formic acid by chromic acid, and it has been proved that in the presence of this salt the temperature coefficient is appreciably higher than that in the absence of the catalyst.

The oxidation of oxalic acid by chromic acid is retarded in the

presence of an excess of sulphuric acid, and the following results are obtained for the temperature coefficient:

N/20-oxalic acid and	Concentration of H_2SO_4	0	3N/5	8N/5	4/N
N/100-chromic acid	and 40° 1	1.96	2.18	2.32	2.66

Thus sulphuric acid, acting as a negative catalyst, produces an increase in the temperature coefficient. Similarly in this oxidation boric acid, molybdic acid, and ammonium molybdate are retarders, and in their presence the temperature coefficient is higher than in their absence.

In the oxidation of sodium formate by mercuric chloride, it has been found that chlorides are retarders, and in their presence the temperature coefficient is appreciably increased. By considering the case of manganese chloride:

Concentration of MnCl ₂	0	0.1722	0.4306	0.8613	1.7726
$k \text{ at } 25^{\circ} \dots \dots$	0.00112	0.000486	0.000207	0.000081	0.000025
Temperature coefficient	4.02	4 ∙06	4 ·2	4.42	4.54

one finds the retarding effect increasing more rapidly than the retarder. Exactly similar results are obtained with zinc chloride.

In the oxidation of sodium formate by silver nitrate, zinc and calcium nitrates have been found to be great retarders, and in their presence the temperature coefficient is higher than that determined in their absence.

In the oxidation of sodium formate by iodine, potassium iodide is a retarder; the temperature coefficient does not practically change in the presence of potassium iodide. This is due, probably, to the following reason. From the work of Taylor (*Proc. Roy. Soc. Edin.*, 1905, **25**, 231; 1908, **28**, 461) on the viscosity of aqueous solutions the following results are obtained:

	Viscosity of	
	N-potassium	Viscosity of
Temperature.	iodide.	water.
_0°	0.854	1.000
15°	0.583	0.640
25°	0.467	0.501

The ratio of the viscosity of water at 25° and $15^{\circ}=0.793$, whilst that of *N*-potassium iodide is 0.801. It is well known that the greater the viscosity, the smaller is the velocity coefficient of a reaction. Evidently in the presence of potassium iodide the ratio of the velocity coefficients at 25° and 15° , that is, the temperature coefficient, would be smaller than that obtained in water. This effect is more pronounced with more concentrated potassium iodide solutions. In the presence of a large excess of potassium iodide, the experimental results show that the tempera-

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Lewis (T., 1914, **105**, 2330; 1915, **107**, 233; 1916, **109**, 796) has studied the hydrolysis of methyl acetate and sucrose in the presence of different concentrations of hydrochloric acid at different temperatures, but in both these cases the difference obtained in the temperature coefficients of a feebly and a strongly catalysed reaction is very small. His results may be explained in the light of the viscosity changes already indicated.

On the other hand, the work of Clark (J. physical Chem., 1907, 11, 353), who has studied the accelerating effect of chromic acid on the interaction of bromic and hydriodic acids, and of Müller (Bull. Soc. Chim., 1911, [iv], 9, 185) on the accelerating effect of hydrochloric acid on the action of iodine on sodium dithionate, shows that the temperature coefficient falls off with the increase in the concentration of the catalysts.

Moreover, Holmberg (Zeitsch. physikal. Chem., 1912, 79, 146) has studied the action of hydroxides of the alkali and alkaline earth metals on the hydrolysis of dibromosuccinic acid, and has found that the greater the acceleration the smaller is the temperature coefficient. The work of de Bruyn and Sluiter (Proc. K. Akad. Wetensch. Amsterdam, 1904, 6, 773) on the transformation of acetophenoneoxime into acetanilide is also in favour of the hypothesis.

This is practically all the literature that is available at present to test this hypothesis. In spite of the fact that numerous catalytic reactions have been investigated, an examination of the literature has shown that in very few cases have catalyst and temperature been varied simultaneously.

In studying the kinetics of the reactions described in this paper the "isolation method" of Ostwald was always used. In the investigation of multimolecular reactions this method has several advantages. By increasing the concentration of one of the reacting substances we can increase the speed so as to bring the reaction within the range of convenient experimental conditions. The oxidation of formic acid by chromic acid is a case in point. The study of the kinetics of the reaction is only possible by having an excess of formic acid; otherwise the reaction is too slow to measure its velocity.

Moreover, by having an excess of one of the reacting substances, the concentration of that reactant does not enter into the question of the velocity, and hence the kinetics become much simpler. VOL. CXI. H H Although the action of chromic acid on tormic acid is a quadrimolecular reaction, in the presence of an excess of the latter acid the reaction follows the unimolecular formula and becomes quite easy to investigate.

In order to study the effect of dilution on temperaturecoefficients, the concentrations of the reacting substances have been widely varied. In the formic acid oxidation, temperature coefficients have been determined using different concentrations of formic acid with a definite concentration of chromic acid. Although, by the change in the concentration of formic acid, the velocity coefficients have widely different values, the temperature coefficients remained practically the same in all cases. Exactly similar results were obtained in the other reactions investigated in this paper. Evidently dilution has no appreciable effect on the equilibrium between "active" and "inactive" molecules. In an important paper Halban (Zeitsch. physikal. Chem., 1909, 67, 176) has shown that unimolecular reactions have larger temperature coefficients than those of multimolecular ones. In addition to the cases enumerated by him, the following are a few more examples in favour of this view. The temperature coefficient of the intramolecular change of acetobromoamide has the value 5.37 between 16° and 25° (van Dam, Rec. trav. chim., 1900, 19, 318), and Kremann (Monatsh., 1910, 31, 245, 1051) has shown that the temperature coefficient of the velocity of decomposition of ethyl hydrogen sulphate in water has the value 4.5 between 55° and 65°. Also Rivett (Zeitsch. physikal. Chem., 1913, 82, 201) has obtained 3.27 for the temperature coefficient of the change of acetochloroanilide to p-chloroacetanilide. Halban's view that reactions which are really multimolecular, but owing to the presence of one of the ingredients in excess appear to be unimolecular, have higher temperature coefficients seems doubtful.

In this investigation it has been shown that the oxidations of formic and oxalic acids by chromic acid follow the unimolecular formula when an excess of formic or oxalic acid is present. Although the reactions are unimolecular, the temperature coefficients are not high, the values being 2.03 for formic acid and 1.94 for oxalic acid between the temperature interval of 25° and 40° . It has already been stated that change in the concentration of formic acid, for example, has no effect on the temperature coefficient. By increasing the concentration of one of the reactants, a bimolecular reaction can be made to appear as a unimolecular one; according to Halban's view, the same reaction will have a temperature coefficient in the unimolecular condition different from that in the bimolecular state. This is not corroborated by experiments. As a matter of fact, the oxidation of potassium oxalate by iodine in the dark is a bimolecular reaction, and has the temperature coefficient 7.2 between 25° and 40° . Similarly, the bimolecular reactions—the oxidation of sodium formate by iodine and by mercuric chloride—have a temperature coefficient of 4.02. It appears, therefore, that the temperature coefficients of both bi- and uni-molecular reactions can be higher than those of multimolecular reactions.

In a similar way Hirniak's work (Chem. Zentr., 1914, i, 3) on the temperature coefficients of the reaction between dimethylaniline and ethyl iodide can be easily explained. In this investigation it has been shown that under exactly similar conditions the oxidation of oxalic acid by chromic acid has a greater velocity and smaller temperature coefficient than those of the oxidation of formic acid by chromic acid. Similar results have been obtained by Kremann (loc. cit.) and Hirniak (loc. cit.). From their work it can be seen that, when the order of the reactions considered is the same, those with greater velocities have smaller temperature All these facts, and the deduction of Skrabal coefficients. Monatsh., 1914, 35, 1157; 1916, 37, 191) that immeasurably rapid reactions have a temperature coefficient of unity, can be easily understood on the basis of the hypothesis of "active" and "inactive" molecules, since an immeasurably rapid reaction is possible when the number of "active" molecules are very large, and this being the case, temperature will have very little effect on this reaction.

Recently a purely physical concept of active molecules has been introduced by Marcelin (Compt. rend., 1914, **158**, 161) and Rice (Brit. Assoc. Report, 1915, 397). By treating the problem of reaction velocity from the point of view of statistical mechanics, they have correlated the reaction velocity with the temperature on the assumption that only those molecules react which reach a "critical" condition, in which they acquire a certain energy considerably in excess of the average energy per molecule of the system.

Rice's equation is

$$\frac{d\log k}{dT} = \frac{Vc - Vm + \frac{1}{2}RT}{RT^2},$$

where Vm is the mean potential energy of the molecular group in question, so that Vc - Vm is the "critical" increment of energy necessary for the reaction.

The forces involved are supposed to be electromagnetic, and therefore subject to modification due to change of radiation density produced by a catalyst. This leads to the conclusion that a positive catalyst, by reducing Vc - Vm, increases k, but decreases $d \log k/dT$, and vice versâ for a negative catalyst. These deductions are in agreement with the experimental results brought forward in this paper.

Furthermore, in a recent experimental paper on the photochemical changes occurring in aqueous solutions of chloroplatinic acids, Boll (Ann. Physique, 1914, [ix], **2**, 5, 226) has concluded from his work that there exist intermediate active phases of the reacting molecules. Goldschmidt (Physikal. Zeitsch., 1909, **10**, 206, 421), from theoretical considerations, also draws a similar conclusion. Moreover, the recent work by Baly and his pupils (T., 1908, **93**, 2108; 1912, **101**, 1469, 1475) on the absorption spectra of compounds has experimentally proved the existence of those very active phases of molecules as intermediate stages in chemical reactions such as advocated in this paper.

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