THE KINETICS OF THE REACTION BETWEEN

POTASSIUM PERMANGANATE AND

OXALIC ACID

Thesis by

Herbert F. Launer.

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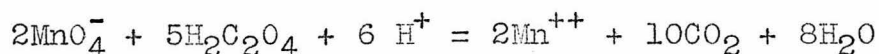
California Institute of Technology,

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THE KINETICS OF THE REACTION BETWEEN
POTASSIUM PERMANGANATE AND OXALIC ACID I.

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INTRODUCTION

The overall reaction between permanganate and oxalic acid is expressed by the equation:

$$2MnO_4^- + 5H_2C_2O_4 + 6\ H^+ = 2Mn^{++} + 10CO_2 + 8H_2O$$

The rate of this reaction has been studied by several investigators

Harcourt and Esson, Phil.Trans.,1866, 201; Schilow, Ber., 36, 2753 (1903); Skrabal, Z. anorg. Chem., 42, 1 (1904).

all of whom used an iodimetric method for the analysis of the reaction mixtures.

In this paper are presented the results of a new investigation of the reaction between permanganate ions and oxalate ion.

A large number of experiments were made on this reaction by an improved method which show that the mechanism previously suggested by Skrabal is not consistent with all of the experimentally found facts. Because of the rather complicated nature of the reaction the outstanding experimental results and theoretical conclusions will, for greater clearness, be stated briefly at this point.

When a solution of permanganate ion is added to one of manganous ion in which acid and oxalate ion are also present a cherry-red solution of a complex ion formed from manganic ion and oxalate ion results, whereas in the absence of oxalate ion or
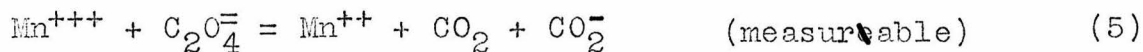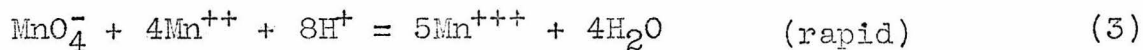
other
anion capable of forming a complex, a precipitate of manganese
dioxide is obtained. It will be shown that the formula of the
manganic complex ion is $Mn(C_2O_4)_2^-$.

The rate of the reaction when manganous ion was present
initially in excess and when the solution was in contact with a
constant gas space was found to be represented by the following
differential equation:

$$\frac{dp_{CO_2}}{dt} = \frac{k_1(Mn(C_2O_4)_2^-)}{(C_2O_4^=)} \tag{2}$$

The following series of reactions provides a mechanism
that is in accord with equation (2).

$$MnO_4^- + 4Mn^{++} + 8H^+ = 5Mn^{+++} + 4H_2O \qquad \text{(rapid)} \tag{3}$$

$$Mn^{+++} + 2C_2O_4^= = Mn(C_2O_4)_2^- \qquad \text{(rapid, reversible)} \tag{4}$$

$$Mn^{+++} + C_2O_4^= = Mn^{++} + CO_2 + CO_2^- \qquad \text{(measurable)} \tag{5}$$

$$Mn^{+++} + CO_2^- = Mn^{++} + CO_2 \qquad \text{(rapid)} \tag{6}$$

It will be noted that the existence of an unknown ion CO_2^- is postu-
lated in equation 5 - a matter which is further considered below.
Reaction 3 is to be regarded in the present connection only as the
source of tripositive manganese, the concentration of whose ion
(Mn^{+++}) is determined by the equilibrium conditions of reaction 4.
This reaction also involves the concentration of oxalate ion, which
is itself dependent upon the acidity of the solution. The rate of
the reaction is then determined by reaction 5, whose rate should be
expressed by the equation:

$$\frac{dp_{CO_2}}{dt} = k_2(Mn^{+++})(C_2O_4^=). \tag{7}$$

By substituting for (Mn^{+++}) in equation 7 the expression $\frac{1}{k_4}(Mn(C_2O_4)_2^-)/(C_2O_4^=)^2$ given by the mass-action law, there results equation 2, which was found to express the experimental results.

This mechanism is in sharp contrast with that of Skrabal, which required that the measureable step be the dissociation of a manganic-oxalate complex, and that the reaction in which manganic ion is reduced be rapid, and of third order.

This and all other drawings will be cut from the magazine article (J.A.C.S. June 1932) and inserted into these spaces as soon as the reprints reach me.

H. F. Launer

For Fig I, See Reverse of Fig II.

METHOD OF EXPERIMENTATION

An apparatus for measuring the pressures of carbon dioxide produced was constructed and is shown diagramatically in Fig. 1. Into the reaction vessel were placed 90 cc. of solution,

containing all but one of the reactants. Since the apparatus is rigid above the thermostat, a jar, kept overflowing with water from the thermostat may be raised so that C is surrounded by water of the desired temperature. The stirrer A is so constructed that it not only churns the liquid but also forces the vapor phase through the liquid. The stirrer is connected to the system by means of the mercury seal K which is so designed that the maximum increase in pressure, accompanied by a difference in mercury levels in the seal, will cause a negligibly small increase (less than 1%) in the volume of the vapor phase.

From the buret 10 cc. of the last reactant were then introduced, the stopcock F, was closed, and readings were taken on the water manometer at suitable intervals. The reservoir D contains the water that must be forced up the manometer tube on the scale G in order that the hydrostatic pressure balance the gas pressure in C, and that the meniscus I return to its initial position.

The pressures p_{CO_2} of carbon dioxide as read on the manometer are proportional to the number of mols of carbon dioxide evolved in the reaction, inasmuch as carbon dioxide obeys Henry's law at pressures of one tenth atmosphere and inasmuch as the volume and temperature are essentially constant. The total pressure in the system was always in the neighborhood of one atmosphere.

A series of blank experiments in which the rate of stirring was varied over wide limits above a certain high value all gave the same curve, showing that equilibrium between the gas and liquid phases was established with sufficient rapidity.

Baker's Analyzed "C.P" chemicals were used throughout. All experiments were carried out at $25.14 \pm 0.02^\circ$. Although most of the specific reaction rates show some trend, yet a comparison of the slopes at corresponding points on two curves (representing systems which differ only in the concentration of one component) allows conclusions to be drawn as to the effect of that component on the reaction rate, and as to the order of the reaction with respect to that component.

THE EXPERIMENTS

(With the exception of one series all rate data are grouped at the end of this article).

present served to reduce the permanganate as rapidly as the latter could be added, with the formation of a cherry-red solution.
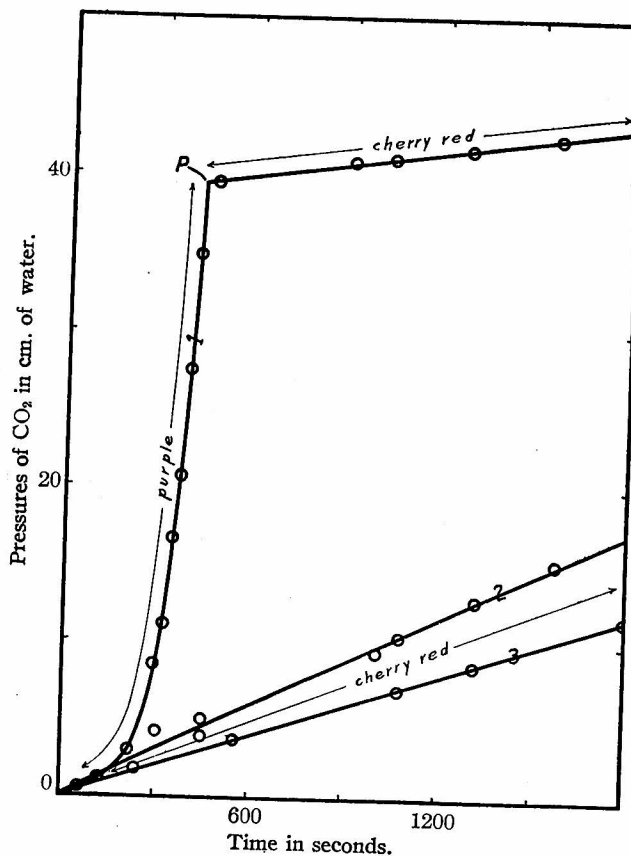

Fig. 2.—The effect of manganous ion and acid.

Formula weights in 1312 liters of solution

| Experiment	KMnO₄	H₂SO₄	K₂C₂O₄	MnSO₄
1	1	98.4	246	0
2	1	98.4	246	13
3	1	72.2	246	13

The typical "induction" curve, curve (1), Fig. II, (corresponding to experiment (1)) was obtained when no manganous ion was initially added. As indicated, point P is coincident with an abrupt color change in the solution. The abrupt simultaneous changes of rate and color make it seem reasonable that curve (1) from O to P represents at least three changes in the oxidation states of manganese; one from permanganate to some intermediate state; another, from the intermediate state to the manganic state; and the third, from the manganic state to the manganous state. From point P to the end, however, the curve seems to represent only the change from the manganic to the manganous state, the steadily increasing manganous ion concentration having served to eliminate all stages of manganese higher than the tripositive one.

THE EXISTENCE OF THE MANGANIC OXALATE AND FLUORIDE COMPLEXES

In experiment (2), represented by curve (2), Fig. II, the manganous ion initially present served to reduce the permanganate as rapidly as the latter could be added, with the formation of a cherry-red solution.

To prove that the cherry-red color is due to tripositive manganese the following experiment was performed. Two equal portions of permanganate solution were treated with an excess of manganous ion in slightly acid solution. The manganese dioxide precipitates were each filtered and washed free from manganous ion. One portion was placed in an acidified potassium iodide solution and the liberated iodine titrated with thiosulfate, of which 20.10 cc.

were required. The other portion was placed in a solution of
sulfuric acid and potassium oxalate like that of experiment (1).
The manganese dioxide dissolved rapidly and gave a cherry-red
solution, indistinguishable in color from those previously observed.
Potassium iodide was immediately added and the iodine titrated,
using this time 9.95 cc. of thiosulfate. The tetrapositive man-
ganese evidently lost one-half of its oxidizing power and was con-
verted, therefore, into the manganic state, the latter being re-
sponsible for the color observed above. The reaction that took
place was evidently,

$$2MnO_2 + (2n+1)C_2O_4^= = 2Mn(C_2O_4)_n^- + 2CO_2 \qquad (8)$$
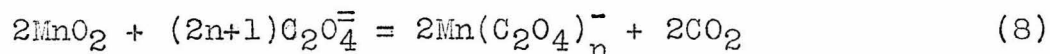
Next, freshly precipitated manganese dioxide was introduced
into an acidified solution of potassium fluoride. No manganese
dioxide dissolved until manganous ion was added, whereupon the rapid
reaction

$$4H^+ + MnO_2 + Mn^{++} = 2 Mn^{+++} + 2H_2O \qquad (9)$$
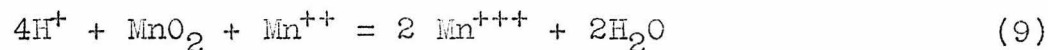
doubtless took place with the subsequent formation of a manganic
fluoride complex.

THE EFFECT OF ACID, OXALATE ION, AND
MANGANIC ION ON THE REACTION RATE

A comparison of curves (2) and (3), Fig. II, shows the
effect of acid on the rate. It is to be noted, however, that the
concentration of oxalate ion is inversely proportional to the con-
centration of hydrogen ion, since oxalic acid is weak. The follow-
ing experiments show that acid is without influence on the rate if
the concentration of oxalate ion is fixed: A buffer, consisting of

a mixture of acetic acid and ammonium acetate, served to maintain constant the concentration of the oxalate ion. The concentration of hydrogen ion could be varied four-fold, while that of the oxalate ion remained essentially constant.
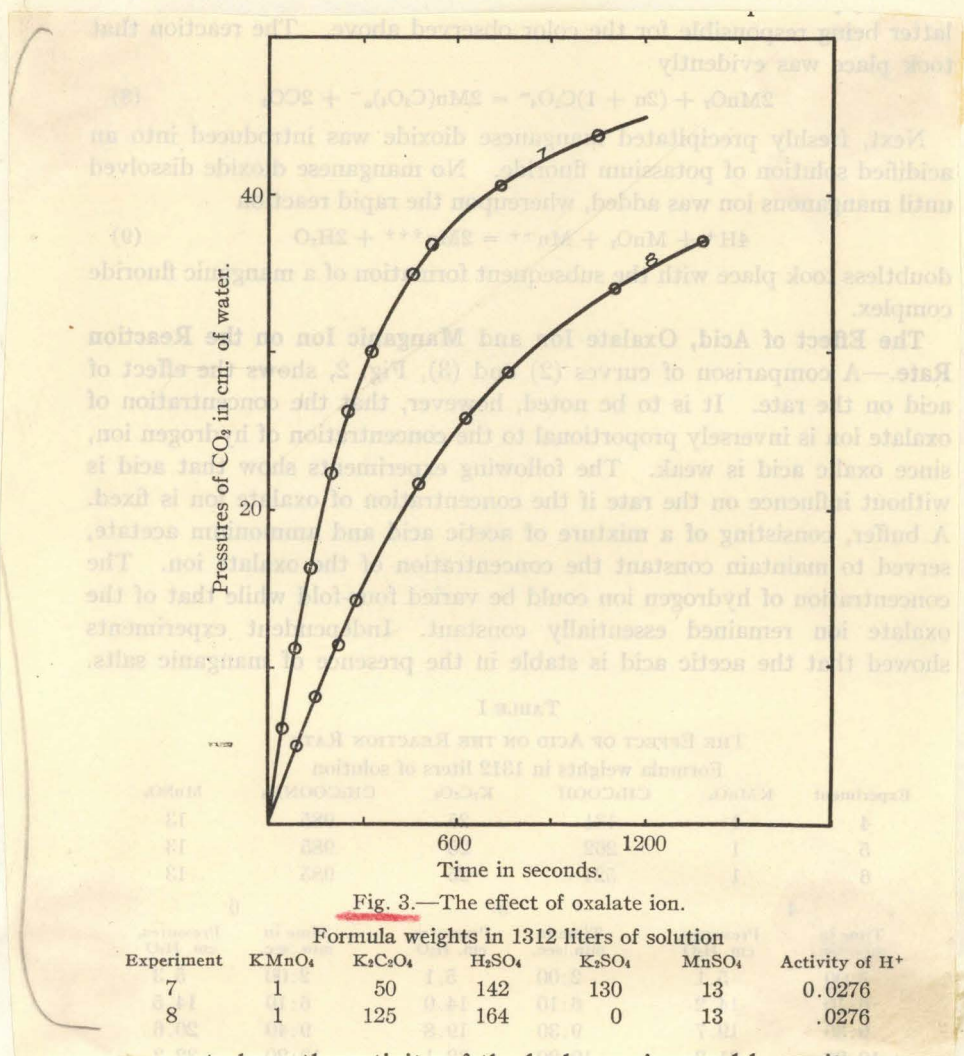
TABLE I

The Effect of Acid on the Reaction Rate

Formula Weights in 1312 liters of solution

Experiment	$KMnO_4$	CH_3COOH	$K_2C_2O_4$	CH_3COONH_4	$MnSO_4$
4	1	131	25	985	13
5	1	262	25	985	13
6	1	524	25	985	13

4		5		6	
Time Min:secs	Pressures cm. H_2O	Time Min:secs	Pressures cm. H_2O	Time Min:secs	Pressures cm. H_2O
2 : 00	5.1	2 : 00	5.1	2 : 00	5.3
6 : 10	14.2	6 : 10	14.0	6 : 10	14.5
9 : 30	19.7	9 : 30	19.8	9 : 40	20.6
19 : 20	31.2	19 : 20	32.1	19 : 20	32.3
24 : 00	35.1	24 : 00	36.2	24 : 00	36.5
28 : 30	38.1	28 : 30	38.8	28 : 30	39.2

The rates vary only 1-2% while the acidity varies 200%, the concentration of oxalate ion remaining essentially constant. The results show that the effect of acid upon the rate is due solely to its effect on the concentration of oxalate ion.

A series of experiments was made in which the acidity and ionic strength were maintained constant while the concentration of oxalate ion was varied. In preliminary experiments the quinhydrone electrode was used to determine the relative proportions of sulfuric acid and potassium oxalate necessary to keep the activity of the hydrogen ion, and hence its concentration, constant. The potassium

sulfate was used to adjust the ionic strength of the solution. In Fig. III the slopes of curve (7) are 2.5 times the slopes of curve (8) at corresponding points, while the concentration of oxalate ion in (8) was 2.5 times that in (7).

Fig. 3.—The effect of oxalate ion.

Formula weights in 1312 liters of solution

Experiment	KMnO$_4$	K$_2$C$_2$O$_4$	H$_2$SO$_4$	K$_2$SO$_4$	MnSO$_4$	Activity of H$^+$
7	1	50	142	130	13	0.0276
8	1	125	164	0	13	.0276

Next, a mixture of potassium sulfate, bisulfate and acid-oxalate was used to keep the acidity fixed but to permit the oxalate ion concentration to vary. In Fig. IV the slopes of curve (9) are twice those of curve (10) and four times those of curve (11) at corresponding points, the concentration of oxalate ion in (10) and (11) being twice and four times respectively that in (9).

Fig. 4.—The effect of oxalate ion.

| Experiment	Formula weights in 1312 liters of solution				
	$KMnO_4$	KHC_2O_4	$KHSO_4$	K_2SO_4	$MnSO_4$
9	1	29	271	200	13
10	1	58	271	200	13
11	1	116	271	200	13
12	0.5	58	271	200	13
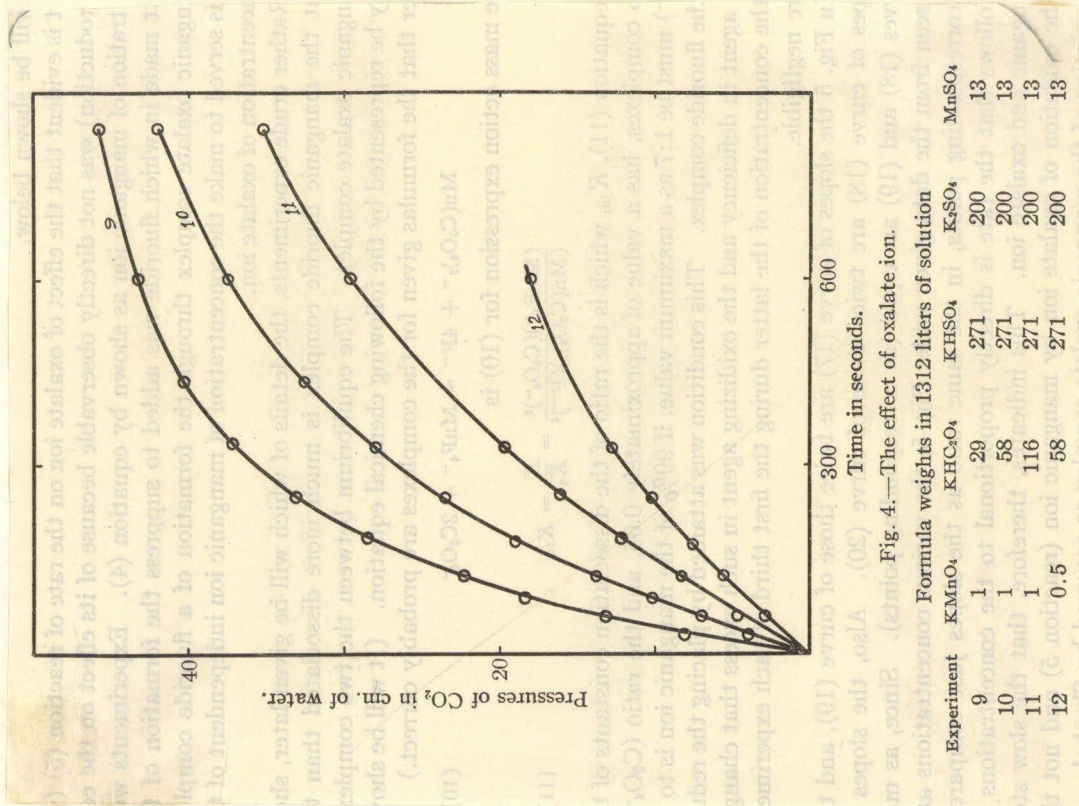
From these results it follows that the rate is inversely proportional to the oxalate ion concentration.

From the results of previous investigators,

Harcourt and Esson, loc. cit.; Skrabal, loc. cit.

and also from the fact that in Fig. IV the slopes of curve (10) are twice those of curve (12), the concentration of oxidizing agent being in the ratio of two to one, it is evident that the reaction is first order with respect to the oxidizing agent. The concentration of the oxidizing agent is essentially equal to the concentration of the complex manganic oxalate anion since this complex dissociates but little, as will be shown below.

It is evident that the effect of oxalate ion on the rate of reaction (5) (see Introduction) was not directly observable because of its effect on the concentration of manganic ion as shown by equation (4). Experiments were next made in which fluoride was added to suppress the formation of the manganic oxalate complex through the formation of a fluoride complex. This served to make the concentration of manganic ion independent of the concentration of oxalate ion.

Rather crude experiments, the details of which will be given later, show that the manganic fluoride complex is much more dissociated than the manganic oxalate complex. The equilibrium between the two complexes may be represented by the following chemical equation. (It will be shown later that the formulae given for the complexes are probably correct).

$$Mn(C_2O_4)_2^- + 4F^- = MnF_4^- + 2C_2O_4^= \tag{10}$$
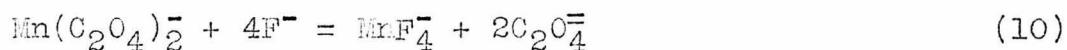
The mass-action expression for (10) is

$$\frac{(MnF_4^-)(C_2O_4^=)^2}{(Mn(C_2O_4)_2^-)(F^-)^4} = \frac{K}{K_4} = K_{10} \tag{11}$$

In equation (11), K_{10}, which is the ratio of the dissociation constants of the two complexes, has a value of approximately 0.05, and the ratio $(C_2O_4^=):(F^-)$ must be 1:7 as a maximum value, if 99% of the manganic ion is to be in the fluoride complex. This condition was attained by placing the reducing agent in deficiency and the oxidizing agent in such excess that changes in the concentration of the latter during the first third of each experiment were negligible.

In Fig. V the slopes of curve (17) are twice those of curve (19), and the slopes of curve (18) are twice those of curve (20). Also, the slopes of curves (18) and (19) are equal (at corresponding points). Since, as may be seen from the data given under Fig. V, the various concentrations are, at corresponding points, in the same ratio as the slopes just compared, it follows that the rate is directly proportional to the concentrations of manganic and oxalate ion. This indicates, therefore, that the slow step is the **oxidation of oxalate ion by manganic ion (reaction 5)** and not the dissociation of the manganic oxalate complex as assumed by Skrabal.
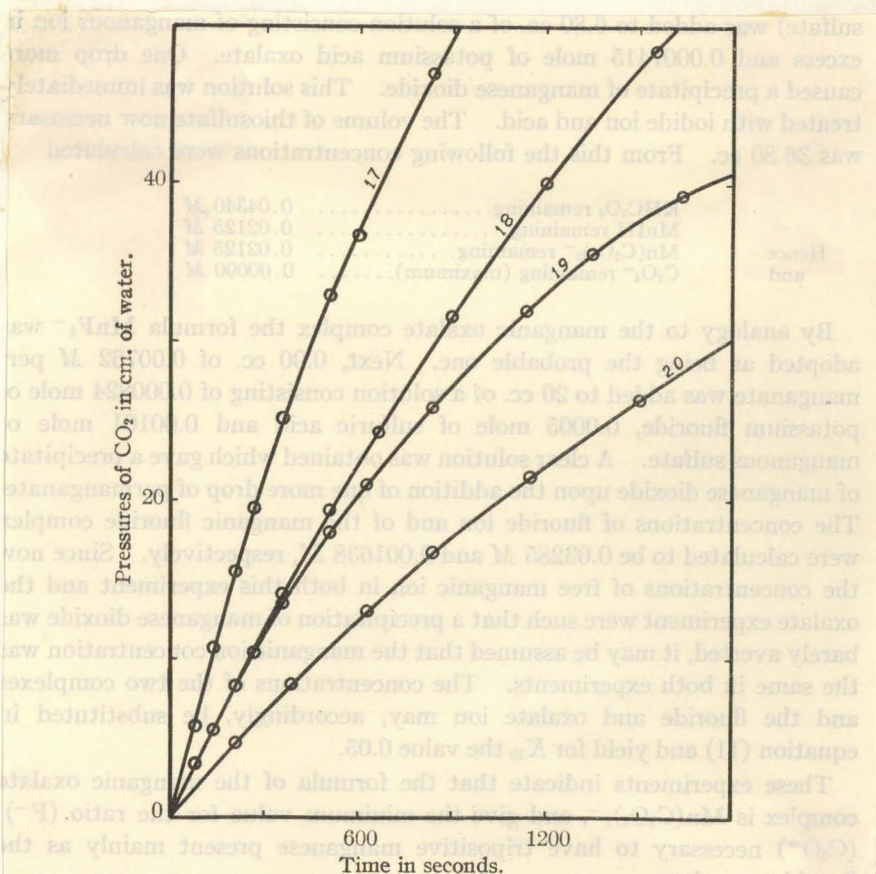

Fig. 5.—The effect of oxalate ion when tripositive manganese is present principally as a complex fluoride.

Formula weights in 647 liters of solution

Experiment	KHC₂O₄	KMnO₄	MnSO₄	KF	KHSO₄	(NH₄)₂SO₄
17	2	2.36 (6-fold excess)	26	155	201	65
18	2	1.18 (3-fold excess)	13	155	201	65
19	1	2.36 (12-fold excess)	26	155	201	65
20	1	1.18 (6-fold excess)	13	155	201	65

THE MANGANIC OXALATE AND FLUORIDE COMPLEXES

Aside from reaction-rate data it is desirable to prove that the formula of the manganic oxalate complex is $Mn(C_2O_4)_2^-$.

The following experiments were based on the fact that if the concentration of manganic ion exceeds a certain value manganese dioxide will precipitate. In each experiment was determined the concentration of oxalate or fluoride ion necessary to prevent the formation of manganese dioxide from a given amount of permanganate, manganous ion and sulfuric acid.

Equal portions of permanganate were added to solutions consisting of an excess of acid and of manganous ion, and of varying amounts of potassium oxalate such that the ratio: mols of $K_2C_2O_4$: mols of tripositive manganese was 1.00, 1,25, 1.5, 1.75, 1.875, and 2.00. Only in the last case was a clear solution obtained, thus showing that two oxalate ions combine with one manganic ion to form the complex.

With this information the following experiments were carried out. Ten (10.00) cc. of 0.00762 $\underline{M}$ permanganate (equivalent to 39.20 cc. thiosulfate) were added to 6.80 cc. of a solution consisting of manganous ion in excess and 0.0007415 mol potassium acid oxalate. One drop more caused a precipitate of manganese dioxide. This solution was immediately treated with iodide ion and acid. The volume of thiosulfate now necessary was 36.80 cc. From this were calculated the following concentrations:

KHC_2O_4 remaining - - - - 0.04340 M

Mn^{III} "   - - - - 0.02125 $\underline{M}$

Hence, $Mn(C_2O_4)_2^-$ remaining - - - - 0.02125 $\underline{M}$

and $C_2O_4^=$ "   - - - - 0.00090 $\underline{M}$ *(maximum)*

By analogy to the manganic oxalate complex the formula MnF_4^- was adopted as being the probable one. Next, 0.90 cc. of 0.00762 $\underline{M}$ permanganate were added to 20 cc. of a solution consisting of 0.000824 mol potassium fluoride, 0.0005 mol sulfuric acid, and 0.00101 mol manganous sulfate. A clear solution was obtained which gave a precipitate of manganese dioxide upon the addition of one more drop of permanganate. The concentrations of fluoride ion and of the manganic fluoride complex were calculated to be 0.03285 $\underline{M}$ and 0.001638 $\underline{M}$ respectively. Since now the concentrations of free manganic ion in both this experiment and the oxalate experiment were such that a precipitation of manganese dioxide was barely averted, it may be assumed that the manganic ion concentration was the same in both experiments. The concentrations of the two complexes and the fluoride and oxalate ion may, accordingly, be substituted in equation (11) and yield for K_{10} the value 0.05.

These experiments indicate that the formula of the manganic oxalate complex is $Mn(C_2O_4)_2^-$, and give the minimum value for the ratio $(F^-):(C_2O_4^=)$ necessary to have manganic manganese present mainly as the fluoride complex.

In the following experiments, (21) and (22), Fig. VI, the oxalate ion concentration remained unchanged, but the acid-oxalate ion concentration varied five-fold. The slight difference in rate indicates that it is the oxalate ion, and not the acid-oxalate ion which forms the complex and which reacts as in equation (5).
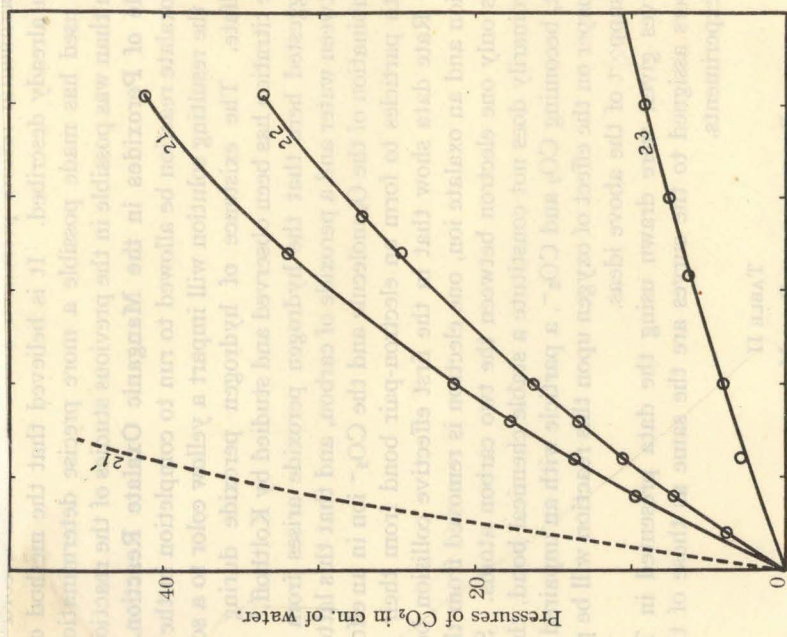
Fig. 6.—The effect of binoxalate ion and the ionic strength on the rate.

Experiment	KMnO₄	K₂C₂O₄	KHC₂O₄	(NH₄)₂SO₄	MnSO₄	Ionic strength
			Formula weights in 1312 liters of solution			
21	1	49	28	1310	13	3.26
22	1	49	140	1310	13	3.26
23	1	49	140	0	13	0.26

Curve (21), Fig. VI would represent approximately the
rate in experiment (21) if the acid-oxalate ion were the principal
complex-former.

THE EFFECT OF IONIC STRENGTH ON THE RATE

In the foregoing experiments precautions were taken to
minimize changes in rate due to changes in the ionic strength. A
comparison between the curves for experiments (22) and (23), Fig.VI,
which differ only in ionic strength, shows that there is a large
positive salt effect on the rate. The change in rate was approxi-
mately 500% while the change in the solubility of carbon dioxide
was small, 15%, compared to this. When modified by Brönsted's rate
hypothesis the experimentally determined rate equation (2) becomes

$$\frac{dp_{CO_2}}{dt} = \frac{k(Mn(C_2O_4)_2^=)}{(C_2O_4^=)} \cdot \frac{f_1}{f_2 \quad f_3} \tag{18}$$

where f_1, f_2, and f_3 are the activity coefficients of the manganic oxalate complex, the oxalate ion, and the unipositive critical complex ion respectively. This expression, after cancellation of the activity coefficients of the two singly charged ions, evidently requires that the rate increase rapidly with the ionic strength and this was found experimentally to be the case.

The experimental results presented above are all in accord with the mechanism already described. It is believed that the method of experimentation used has made possible a more precise determination of the mechanism than was possible in the previous studies of the reaction.

THE ROLE OF PEROXIDES IN THE MANGANIC OXALATE REACTION

If the manganic-oxalate reaction be allowed to run to completion in the presence of oxygen the resulting solution will impart a yellow color to a solution of titanic sulfate. The existence of hydrogen peroxide during the permanganate titration has been observed and studied by Kolthoff.

Kolthoff, Z. anal. Chem., 64, 185 (1924).

It is suggested here that the hydrogen peroxide arises from an equilibrium between water and a peroxide of carbon, and that this latter results from a combination of the O_2 molecule and

the CO_2^- ion in an effort on the part of both particles to form an electron pair bond from their unpaired electrons. Rate data show that in the first effective collision between a manganic ion and an oxalate ion, one electron is removed from the latter. This leaves only one electron between the two carbon atoms. Since one electron ordinarily does not constitute a stable chemical bond, the carbon atoms part, becoming CO_2 and CO_2^-, a particle with an unpaired electron. In a later paper on the effect of oxygen upon this reaction will be presented results in support of the above ideas.

TABLE II

RESULTS OF THE RATE MEASUREMENTS

Experiment (1) Time in Min:sec	Press.CO_2 in cm.H_2O	Experiment (2) Time in Min:sec	Press.CO_2 in cm.H_2O	Experiment (3) Time in Min:sec	Press.CO_2 in cm.H_2O	Experiment (7) Time in Min:sec	Press.CO_2 in cm.H_2O
1 : 00	0.5	3 : 45	2.9	4 : 00	1.8	0 : 45	6.1
2 : 00	1.2	5 : 05	4.2	7 : 30	3.9	1 : 25	11.2
3 : 40	3.0	7 : 30	5.0	18 : 00	7.0	2 : 25	18.0
4 : 50	8.5	16 : 45	9.4	22 : 00	8.6	3 : 20	22.3
5 : 20	11.1	18 : 00	10.4	30 : 00	11.7	4 : 15	26.2
5 : 40	15.1	22 : 00	12.7	45 : 00	17.1	5 : 30	30.0
6 : 05	20.6	26 : 15	15.2	55 : 00	20.3	7 : 40	34.9
6 : 30	27.4	30 : 00	17.1			8 : 40	36.8
6 : 55	34.8	42 : 30	22.9			12 : 20	40.6
7 : 45	39.4	45 : 50	24.2			17 : 30	43.8
15 : 00	40.8	51 : 30	26.4				
17 : 10	41.0	56 : 10	28.4				
21 : 15	41.6						
26 : 00	42.4						
∞	(60.2)	∞	60.2	∞	(60.2)	∞	48.0

(8)		(9)		(10)		(11)	
0 : 40	2.6	0 : 30	8.1	0 : 30	4.0	0 : 30	2.6
1 : 30	5.0	1 : 00	13.2	1 : 00	7.0	1 : 00	4.7
2 : 30	8.1	1 : 30	18.4	1 : 30	10.2	1 : 30	6.2
3 : 45	11.4	2 : 05	22.3	2 : 05	13.8	2 : 05	8.3
4 : 40	14.2	3 : 05	28.5	3 : 00	19.0	3 : 05	12.2
8 : 00	21.6	4 : 10	33.1	4 : 10	23.5	4 : 15	16.1
10 : 30	25.8	5 : 35	37.2	5 : 30	28.0	5 : 30	19.7
12 : 45	28.7	7 : 15	40.3	7 : 15	32.6	10 : 00	29.6
18 : 25	34.1	10 : 50	43.3	10 : 00	37.5	14 : 00	35.2
23 : 05	37.1	14 : 00	45.8	14 : 00	42.0		
∞	(48.0)	∞	47.0	∞	(47.0)	∞	(47.0)

(20)		(21)		(22)		(23)	
1 : 20	1.9	4 : 00	9.7	1 : 00	2.1	6 : 00	2.9
2 : 30	3.6	6 : 00	13.6	2 : 00	3.8	10 : 00	4.0
3 : 30	4.7	8 : 00	17.7	4 : 00	7.2	16 : 00	6.2
4 : 30	5.8	10 : 00	21.3	6 : 00	10.5	20 : 00	7.5
6 : 30	8.4	17 : 00	32.0	8 : 00	13.3	25 : 00	9.1
10 : 30	13.0	19 : 00	34.5	10 : 00	16.2	30 : 00	10.9
14 : 00	16.7	25 : 30	41.2	17 : 00	24.7		
19 : 10	21.5			19 : 00	27.2		
25 : 00	26.4			21 : 00	29.2		
31 : 00	31.0			25 : 30	33.6		
∞	(52)	∞	55	∞	(55)	∞	47

The curves given above were drawn using the data presented in this table. The numbers assigned to the curves are the same as those of the corresponding experiments.

SUMMARY

An apparatus was designed for the measurement of rapid reactions in solutions involving even exceedingly small quantities of gaseous product (0.02 millimols) provided either that this gas follow Henry's law or that the deviations therefrom be known.
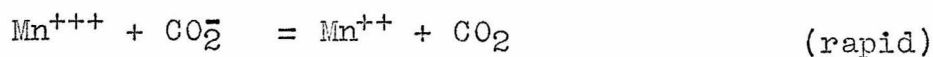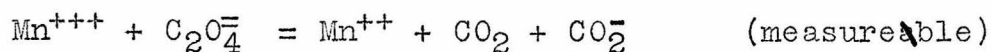
The reaction between tripositive manganese and oxalate ion has been studied and found, in agreement with the work of previous investigators, to be an important step in the reaction between permanganate and oxalic acid. The rate of this reaction was found to be expressible by the equation

$$\frac{dp_{CO_2}}{dt} = K\frac{(Mn(C_2O_4)_2^-)}{(C_2O_4^=)}$$

when oxalate ion is in excess, and by the equation

$$\frac{dp_{CO_2}}{dt} = k \ (Mn^{+++})(C_2O_4^=)$$

when oxalate ion is in deficiency and fluoride ion is present to form a complex with manganic ion. This led to the adoption of the following mechanism.

$$Mn^{+++} + 2C_2O_4^= = Mn(C_2O_4)_2^- \qquad \text{(rapid, reversible)}$$
$$Mn^{+++} + C_2O_4^= = Mn^{++} + CO_2 + CO_2^- \qquad \text{(measureable)}$$
$$Mn^{+++} + CO_2^- = Mn^{++} + CO_2 \qquad \text{(rapid)}$$

The formula of the manganic oxalate complex ion was found to be $Mn(C_2O_4)_2^-$.

The influence of the ionic strength on the rate was found to be in accord with that predicted using the Brønsted hypothesis.

An explanation was proposed for the formation of peroxides when the reaction takes place in the presence of oxygen.

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The writer hopes to present the results of further studies upon the subject in an early issue of the Journal of the American Chemical Society.