has "electronic isomers" which are separated from the basic level by about 160 cm.$^{-1}$ and which have approximately twice the statistical weight of the basic level. These values are in excellent agreement with those calculated in Table II above.

Amelia Frank, *ibid.*, **39**, 119 (1932), in extending the work of J. H. Van Vleck and A. Frank, has attempted an alternative explanation. In view of the experimental facts, her calculations cannot be correct as stated, as her first excited level occurs around 900 cm.$^{-1}$. However, the $^6H_{7/2}$ term would be expected to occur at a slightly greater value than that and at higher temperatures an effect such as they predict probably exists.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 318, AND FROM THE CHEMICAL LABORATORY AT THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

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

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Introduction

The over-all reaction between permanganate and oxalic acid is expressed by the equation

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ = 2Mn^{++} + 10CO_2 + 8H_2O \qquad (1)$$

The rate of this reaction has been studied by several investigators[1] 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 ion and oxalate ion.

The author wishes to express here his appreciation of the aid and criticisms of Prof. Don M. Yost and Dr. J. B. Ramsey.

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

[1] Harcourt and Esson, *Phil. Trans.*, 201 (1866); Schilow, *Ber.*, **36**, 2735 (1903); Skrabal, *Z. anorg. Chem.*, **42**, 1 (1904).

excess and when the solution was in contact with a constant gas space was found to be represented by the following differential equation

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

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

$MnO_4^- + 4Mn^{++} + 8H^+ = 5Mn^{+++} + 4H_2O$	(rapid)	(3)
$Mn^{+++} + 2C_2O_4^= = Mn(C_2O_4)_2^-$	(rapid, reversible)	(4)
$Mn^{+++} + C_2O_4^= = Mn^{++} + CO_2 + CO_2^-$	(measurable)	(5)
$Mn^{+++} + CO_2^- = Mn^{++} + CO_2$	(rapid)	(6)

It will be noted that the existence of an unknown ion CO_2^- is postulated 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

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

By substituting for (Mn^{+++}) in equation 7 the expression $(1/K_4)(MnC_2O_4^-)/(C_2O_4^=)^2$ 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 measurable 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.

Method of Experimentation

An apparatus for measuring the pressures of carbon dioxide produced was constructed and is shown diagrammatically in Fig. 1. In the reaction vessel was 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 was then introduced, the stopcock F_1 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 moles 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.

All experiments were carried out at 25.14 ± 0.02°. 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 best obtainable materials were used throughout.

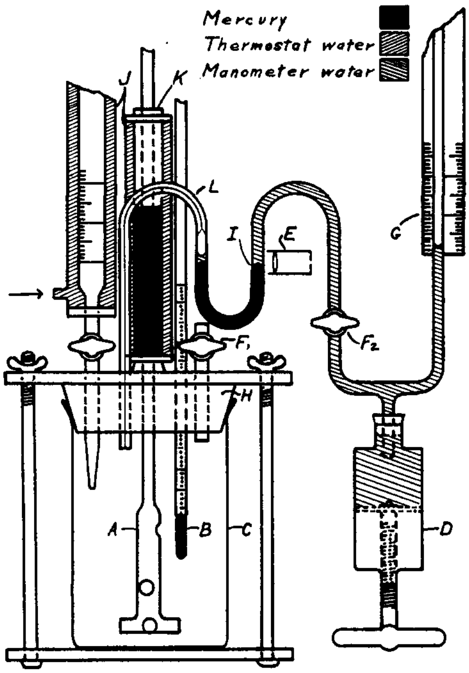

Fig. 1.—Gasometric apparatus: *A*, special centrifuging stirrer; *B*, thermometer; *C*, reaction vessel (a 200 cc. spoutless beaker); *D*, manometer-water reservoir (an "Alemite" grease gun); *E*, small thermometer telescope to observe meniscus I; F_1 and F_2, stopcocks; *G*, meter stick; *H*, rubber stopper, size 12; *I*, meniscus of mercury; *J*, water jackets through which is circulated (by a small pump) water, from thermostat; *K*, mercury seal device; *L*, capillary tubing.

The Effect of Manganous Ion on the Reaction Rate.—With the exception of one series all rate data are grouped at the end of this article.

The typical "induction" curve, curve (1), Fig. 2 (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. 2, 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.

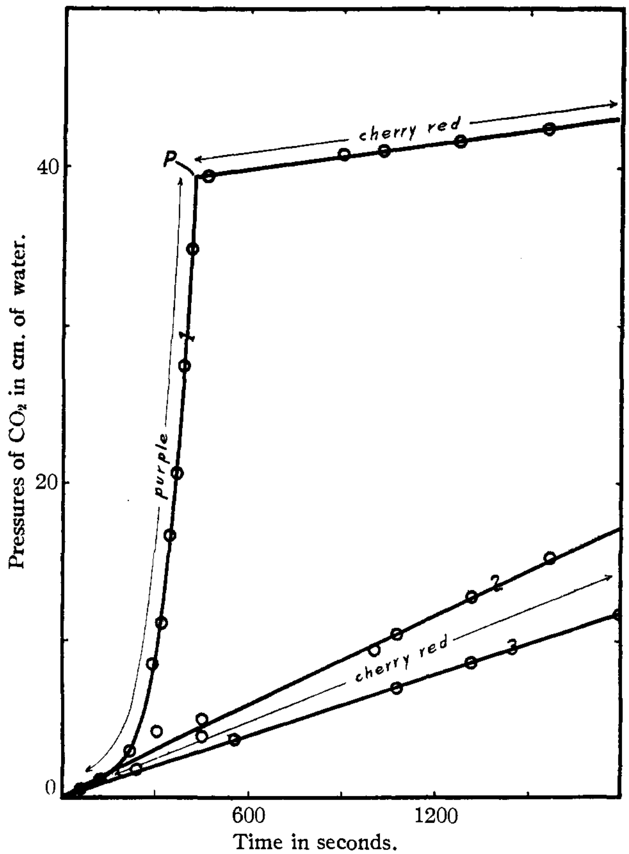

Fig. 2.—The effect of manganous ion and acid.

Formula weights in 1312 liters of solution

Experiment	$KMnO_4$	H_2SO_4	$K_2C_2O_4$	$MnSO_4$
1	1	98.4	246	0
2	1	98.4	246	13
3	1	72.2	246	13

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. was 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 manganese evidently lost one-half of its oxidizing power and was converted therefore into the manganic state, the latter being responsible for the color observed above. The reaction that took place was evidently

$$2MnO_2 + (2n + 1)C_2O_4^{=} = 2Mn(C_2O_4)_n^{-} + 2CO_2 \quad (8)$$

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

$$4H^+ + MnO_2 + Mn^{++} = 2Mn^{+++} + 2H_2O \quad (9)$$

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. 2, 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 concentration of hydrogen ion, since oxalic acid is weak. The following 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. Independent experiments showed that the acetic acid is stable in the presence of manganic salts.

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 in min.:sec.	Pressures, cm. H_2O	Time in min.:sec.	Pressures, cm. H_2O	Time in min.:sec.	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

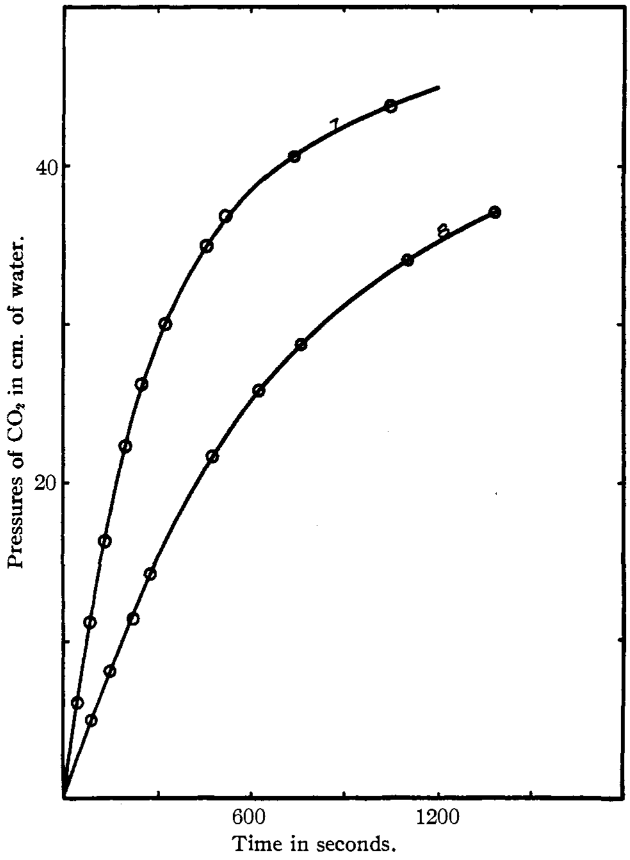

Fig. 3.—The effect of oxalate ion.

Formula weights in 1312 liters of solution

Experiment	$KMnO_4$	$K_2C_2O_4$	H_2SO_4	K_2SO_4	$MnSO_4$	Activity of H^+
7	1	50	142	130	13	0.0276
8	1	125	164	0	13	.0276

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 solutions. In Fig. 3 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).

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. 4 the slopes of curve (9) are twice those of curve (10) and four times those of curve (11) at corresponding points, the concentration

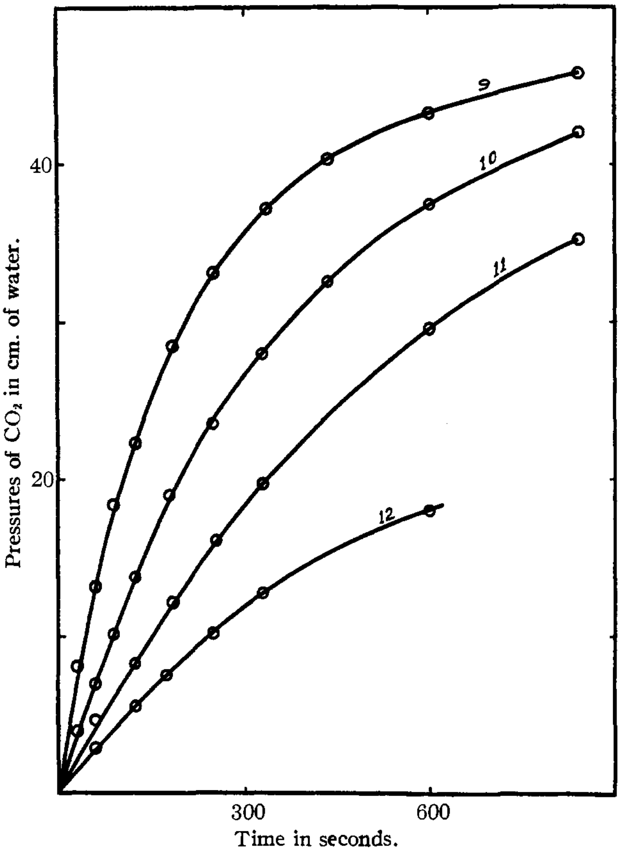

Fig. 4.—The effect of oxalate ion.

Formula weights in 1312 liters of solution

Experiment	$KMnO_4$	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

of oxalate ion in (10) and (11) being twice and four times, respectively, that in (9). From these results it follows that the rate is inversely proportional to the oxalate-ion concentration.

From the results of previous investigators,[1] and also from the fact that in Fig. 4 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 formulas given for the complexes are probably correct.)

$$Mn(C_2O_4)_2^- + 4F^- = MnF_4^- + 2C_2O_4^= \qquad (10)$$

The mass action expression for (10) is

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

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. 5 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. 5, 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.

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.

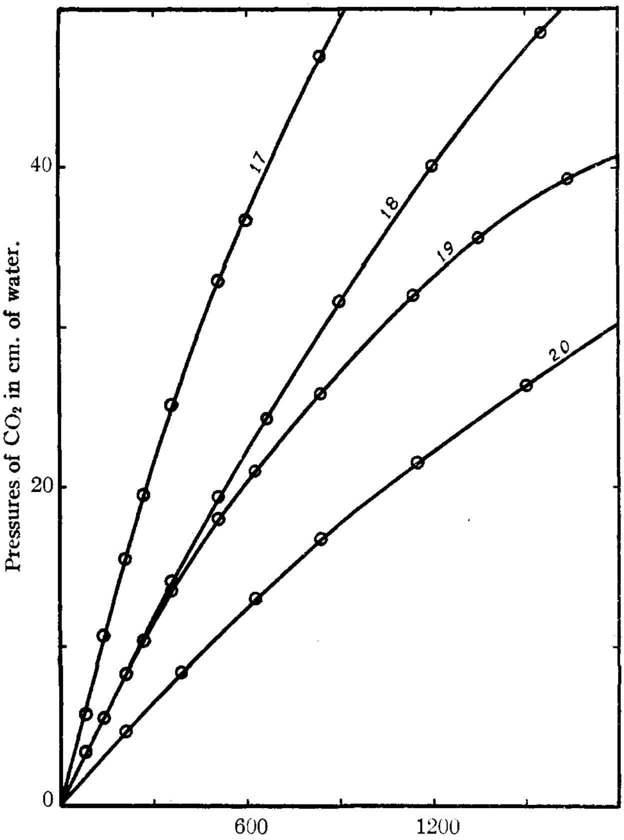

Fig. 5.—The effect of oxalate ion when tripositive manganese is present principally as a complex fluoride.

Formula weights in 647 liters of solution

Experiment	KHC_2O_4	$KMnO_4$	$MnSO_4$	KF	$KHSO_4$	$(NH_4)_2SO_4$
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

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 moles of $K_2C_2O_4$: moles 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 experiment was carried out. Ten (10.00) cc. of 0.00762 M permanganate (equivalent to 39.20 cc. of thiosulfate) was added to 6.80 cc. of a solution consisting of manganous ion in excess and 0.0007415 mole of 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 the following concentrations were calculated

	KHC_2O_4 remaining	0.04340 M
	MnIII remaining	0.02125 M
Hence	$Mn(C_2O_4)_2^-$ remaining	0.02125 M
and	$C_2O_4^=$ remaining (maximum)	0.00090 M

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 M permanganate was added to 20 cc. of a solution consisting of 0.000824 mole of potassium fluoride, 0.0005 mole of sulfuric acid and 0.00101 mole of 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 M and 0.001638 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^-): $(C_2O^=)$ necessary to have tripositive manganese present mainly as the fluoride complex.

In the following experiments, (21) and (22), Fig. 6, 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).

Curve (21′), Fig. 6, 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. 6, which differ only in ionic strength, shows that there is a large positive salt effect on the rate. The change in rate was approximately 500% while the change in the solubility of carbon dioxide was

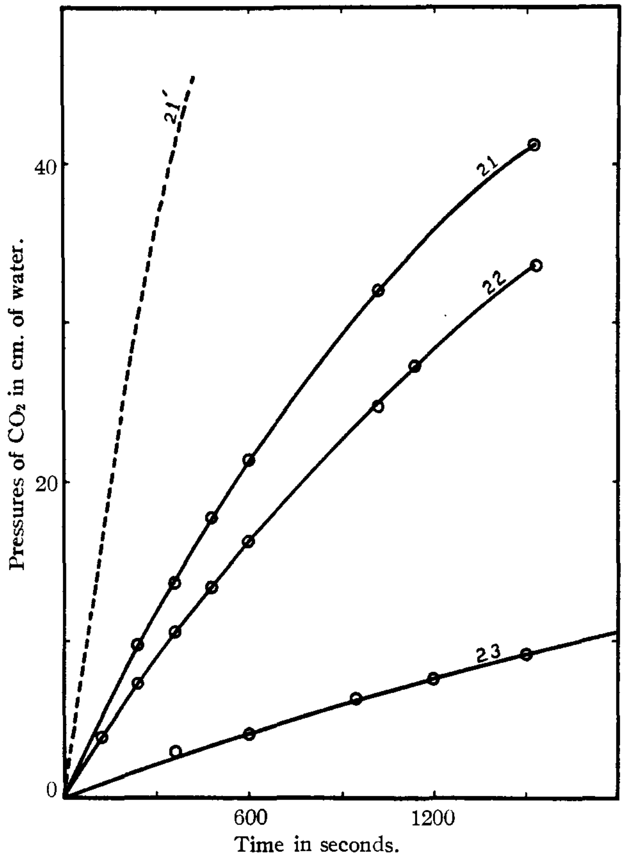

Fig. 6.—The effect of binoxalate ion and the ionic strength on the rate.

Formula weights in 1312 liters of solution

Experiment	$KMnO_4$	$K_2C_2O_4$	KHC_2O_4	$(NH_4)_2SO_4$	$MnSO_4$	Ionic strength
21	1	49	28	1310	13	3.26
22	1	49	140	1310	13	3.26
23	1	49	140	0	13	0.26

small, 15%, compared to this. When modified by Brönsted's rate hypothesis the experimentally determined rate equation (2) becomes

$$\frac{\mathrm{d}p_{CO_2}}{\mathrm{d}t} = \frac{k(Mn(C_2O_4)_2^-)}{(C_2O_4^=)} \cdot \frac{f_1}{f_2 f_3}$$

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.[2]

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.

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

TABLE II

RESULTS OF THE RATE MEASUREMENTS

Experiment (1)		Experiment (2)		Experiment (3)		Experiment (7)	
Time in min.:sec.	Press. CO_2 in cm. H_2O	Time in min.:sec.	Press. CO_2 in cm. H_2O	Time in min.:sec.	Press. CO_2 in cm. H_2O	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	∞	60.2	8:40	36.8
6:35	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			∞	48.0
17:10	41.0	56:10	28.4				
21:15	41.6	∞	60.2				
26:00	42.4						
∞	60.2						

[2] Kolthoff, *Z. anal. Chem.*, **64**, 185 (1924).

Table II (*Concluded*)

(8) Time in min.:sec.	(8) Press. CO_2 in cm. H_2O	(9) Time in min.:sec.	(9) Press. CO_2 in cm. H_2O	(10) Time in min.:sec.	(10) Press. CO_2 in cm. H_2O	(11) Time in min.:sec.	(11) Press. CO_2 in cm. H_2O
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	∞	47.0
∞	48.0	∞	47.0	∞	47.0		
(12)		(17)		(18)		(19)	
0:30	1.5	1:20	5.8	3:30	8.3	1:20	3.4
1:00	2.9	2:20	10.7	6:00	14.1	2:20	5.5
1:30	4.2	3:30	15.5	8:30	19.4	3:30	8.3
2:05	5.6	4:30	19.5	11:05	24.3	4:30	10.4
3:00	7.6	6:00	25.1	15:00	31.6	6:00	13.5
4:10	10.2	8:30	32.9	20:00	40.1	8:30	18.0
5:30	12.8	10:00	36.7	26:00	46.5	10:30	21.0
10:00	18.0	14:00	47.0	30:00	53.7	14:00	25.9
∞	23.5	22:00	63.6	38:00	63.2	19:00	32.0
		∞	104.0	∞	104.0	22:30	35.6
						27:20	39.3
						∞	52.0
(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	∞	47.0
19:10	21.5	∞	55.0	19:00	27.2		
25:00	26.4			21:00	29.2		
31:00	31.0			25:30	33.6		
∞	52.0			∞	55.0		

Summary

An apparatus was designed for the measurement of rapid reactions in solutions involving even exceedingly small quantities of gaseous product (0.02 millimole) 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

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

when oxalate ion is in excess, and by the equation

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

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.

$$\begin{array}{lll} Mn^{+++} + 2C_2O_4^- = Mn(C_2O_4)_2^- & & \text{(rapid, reversible)} \\ Mn^{+++} + C_2O_4^- = Mn^{++} + CO_2 + CO_2^- & & \text{(measurable)} \\ Mn^{+++} + CO_2^- = Mn^{++} + CO_2 & & \text{(rapid)} \end{array}$$

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 Brönsted hypothesis.

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

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITY AND ENTROPY OF CARBON MONOXIDE. HEAT OF VAPORIZATION. VAPOR PRESSURES OF SOLID AND LIQUID. FREE ENERGY TO 5000°K. FROM SPECTROSCOPIC DATA

BY J. O. CLAYTON[1] AND W. F. GIAUQUE

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Carbon monoxide gas is one of the simpler diatomic molecules. Spectroscopically the normal level is a $^1\Sigma$ state and it has no other electronic configurations that are appreciably occupied until temperatures far in excess of the 5000°K. limit of our calculations are reached. While nuclear spin should not produce any appreciable effect on the observed behavior of such a molecule, it is of interest to note that the predominant isotopes of both carbon and oxygen are without nuclear spin.

In view of the molecular simplicity it might be expected that the entropy obtained from the band spectrum would agree with that obtained from the ordinary application of the third law. However, this proves not to be the case and it becomes a matter of considerable practical as well as theoretical interest to determine the extent to which similar effects may exist in other molecules. In attempting to find a definite physical explanation for the discrepancy it is desirable to have an accurate quantitative measure of the amount.

It is also our purpose to consider the equilibrium C (graphite) + $^1/_2O_2$ =

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