309. *The Reaction between Potassium Permanganate and Oxalic Acid, and the Decomposition of Potassium Manganioxalate.*

By JOHN BRADLEY and GORDON VAN PRAAGH.

When potassium permanganate and oxalic acid solutions are mixed, a yellow solution containing a manganioxalate is formed. This salt slowly decomposes into manganous oxalate and carbon dioxide. The object of this work was to examine the nature of this complex ion and its mode of decomposition. The reaction was studied in three parts: (1) the precipitation of manganese dioxide from potassium permanganate and manganous sulphate, (2) the conversion of manganese dioxide into

the manganioxalate by oxalic acid, (3) the self-reduction of this complex. The reduction of the manganese dioxide by oxalic acid was found to be a surface reaction, accompanied by a homogeneous reaction between $\mathrm{Mn^{\cdot\cdot}}$ and $\mathrm{Mn^{\cdot\cdot\cdot\cdot}}$ ions to form $\mathrm{Mn^{\cdot\cdot\cdot}}$ ions. The yellow solution of the complex probably contains the ion

$$\{\mathrm{Mn^{III}(C_2O_4)_2,2H_2O}\}'.$$

Its behaviour was compared with that of the solution obtained from potassium manganioxalate. An equation was obtained for the initial rates of its decomposition in media containing various concentrations of hydrogen ions and oxalic acid, and a mechanism is suggested for its mode of decomposition.

WHEN dilute solutions of potassium permanganate, sulphuric acid, and oxalic acid are mixed, the rate of oxidation of the oxalic acid is slow at first, increases to a maximum, and then decreases again. This behaviour is due to the slow production of manganous sulphate, followed by a rapid reduction of the permanganate, for if manganous sulphate is put into the system at first, the initial slow part of the reaction is eliminated. The colour of the mixed solutions changes through sherry-red, brownish, and yellow to colourless. If acidified potassium iodide solution is added to the reacting mixture, iodine is liberated. In this paper the term " oxidising power of the solution " is used to indicate the quantity of iodine thus set free. Hence, when the solutions are first mixed, the oxidising power is a maximum, and when the mixture has become colourless, it is zero.

This reaction was first studied by Harcourt and Esson (*Phil. Trans.*, 1866, **156**, 193). Skrabal investigated the kinetics (*Ber.*, 1903, **36**, 2735) and concluded that manganic sulphate was formed intermediately by reduction of the permanganate by manganous sulphate, and that the manganic ions formed a complex ion with the oxalate ions, giving the yellow solution, which then slowly decomposed unimolecularly with formation of manganous salts and carbon dioxide. Launer (*J. Amer. Chem. Soc.*, 1932, **54**, 2597; Launer and Jost, *ibid.*, 1934, **56**, 2571) showed that Skrabal's mechanism was inadequate; he followed the course of the reaction by measuring the partial pressure of carbon dioxide evolved, and found that, when the acidity is kept constant by ammonium acetate buffers, the rate of loss of " oxidising power " is inversely proportional to the oxalate-ion concentration, but that when potassium fluoride is added to prevent formation of the manganioxalate complex by forming the more stable manganifluoride, the rate becomes directly proportional to the oxalate-ion concentration. This is in agreement with his mechanism, which is as follows:

$$\mathrm{Mn^{\cdot\cdot\cdot} + 2C_2O_4'' \rightleftharpoons Mn(C_2O_4)_2'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\mathrm{Mn^{\cdot\cdot\cdot} + C_2O_4'' \longrightarrow Mn^{\cdot\cdot} + CO_2' + CO_2}\ \text{(measurable)} \quad . \quad . \quad . \quad (2)$$

followed by $$\mathrm{Mn^{\cdot\cdot\cdot} + CO_2' \longrightarrow Mn^{\cdot\cdot} + CO_2}\ \text{(rapid)} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The rate, determined by (2) if no complex oxalate is formed, is $k[\mathrm{Mn^{\cdot\cdot\cdot}}][\mathrm{C_2O_4''}]$; but if equilibrium (1) exists, $K = [\mathrm{Mn(C_2O_4)_2'}]/[\mathrm{Mn^{\cdot\cdot\cdot}}][\mathrm{C_2O_4''}]^2$, and the rate becomes $k'[\mathrm{Mn(C_2O_4)_2'}]/[\mathrm{C_2O_4''}]$. In his first paper, Launer assumes that the manganic ions are formed by Skrabal's mechanism, *i.e.*, $\mathrm{MnO_4' + 4Mn^{\cdot\cdot} + 8H^{\cdot} \longrightarrow 5Mn^{\cdot\cdot\cdot} + 4H_2O}$, but in his second paper he proves that this does not occur, and concludes that quadrivalent manganese ions are first formed:

$$\mathrm{2MnO_4' + 3Mn^{\cdot\cdot} + 16H^{\cdot} \longrightarrow 5Mn^{\cdot\cdot\cdot\cdot} + 8H_2O, \quad Mn^{\cdot\cdot\cdot\cdot} + Mn^{\cdot\cdot} \longrightarrow 2Mn^{\cdot\cdot\cdot}.}$$

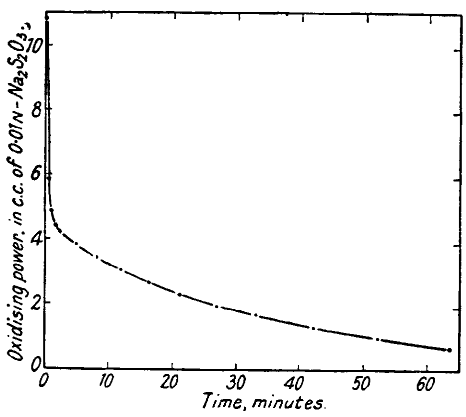
The quadri- and ter-valent manganese ions are assumed to react with the oxalate ions to form ter- and bi-valent manganese ions respectively. These reactions were not isolated, nor was any direct analytical evidence obtained for the existence of the ions $\mathrm{Mn^{\cdot\cdot\cdot\cdot}}$, $\mathrm{Mn^{\cdot\cdot\cdot}}$, or $\mathrm{CO_2'}$.

Lidwell and Bell (J., 1935, 1303) used a simple method for finding the composition of the complex ion. Adding oxalic acid solutions of various concentrations to permanganate–manganous sulphate mixtures after a short interval, they followed the course of the reduction by stopping the reaction by addition of potassium iodide solution. They found an initial fast reaction, followed by a slow unimolecular decomposition, and concluded that the former reduces the composition of the solution to that of the complex; by finding the compositions of the solutions at which the reaction becomes unimolecular, they deduced that the complex ion is $Mn(C_2O_4)_3'''$. We have been unable to confirm this conclusion.

We studied the reaction, at room temperature, by Lidwell and Bell's experimental method. Desiring to segregate the several reactions occurring, we began by noting the effect of varying the interval before adding the oxalic acid solution to the permanganate–manganous sulphate mixture. The rate of oxidation of oxalic acid increases to a maximum as this interval is increased (I).* The increase coincides with the appearance of the red colour in the permanganate–manganous sulphate mixture, and reaches a steady maximum when a brown solid is precipitated. Hence, the latter reacts faster with oxalic acid than does the permanganate–manganous sulphate mixture. The composition of this precipitate is an important clue to the mechanism of the reaction, and it is shown to be a quadrivalent manganese oxide; as its degree of hydration is indefinite, it will be referred to as manganese dioxide. The red colour appearing before the precipitation is probably due to colloidal manganese dioxide. Addition of gum arabic prevents the precipitation by keeping the manganese dioxide in colloidal solution.

The manganese dioxide precipitate is rapidly dissolved by oxalic acid to a yellow solution—both Mn_2O_3 and MnO_2 behave in this manner (III)—and the dissolution is accompanied by a rapid fall in the oxidising power to about half its original value, owing to reduction of the manganese to the tervalent state, which has only half the oxidising power of the quadrivalent state (IV). This reduction corresponds to the steep parts of Lidwell and Bell's curves. The yellow solution thus formed then decomposes comparatively slowly (see Fig. 1).

FIG. 1.



The problem will now be considered in three stages: (1) the production of manganese dioxide from potassium permanganate and manganous sulphate, (2) the reduction of quadri- to ter-valent manganese, and (3) the formation and decomposition of the mangani-oxalate complex.

(1) *The Reduction of Potassium Permanganate by Manganous Sulphate.*—When potassium permanganate and manganous sulphate solutions are mixed in the proportion required by the equation $2MnO_4' + 3Mn'' + 2H_2O \longrightarrow 5MnO_2 + 4H'$, the light brown precipitate appears after a few seconds, and becomes granular and darker on standing. Addition of dilute sulphuric acid retards the reaction and extends the interval before the precipitate first appears (V).

The reaction has been stated to be autocatalytic (Polissar, *J. Chem. Educ.*, 1936, **13**, 40). Our experiments do not show an increase in rate at the beginning of the reaction, but indicate that, before the precipitate appears, there is an induction period which can be eliminated by addition of a finely divided solid. The precipitate granulated sooner if the solution was shaken, and when granular, it reacted more slowly with the oxalic acid than did the fresh precipitate. This suggests that the reaction with the oxalic acid occurs on the surface, and this is supported by other evidence (see Fig. 2).

(2) *The Conversion of Manganese Dioxide into the Manganioxalate Ion.*—The study of this part of the reaction leads to two main conclusions: (*a*) that the reaction between oxalic acid and manganese dioxide takes place on the surface of the latter, and (*b*) that the quadrivalent manganese can be reduced to tervalent by bivalent manganese, a reaction which is probably homogeneous and ionic.

The result of adding oxalic acid solution to a suspension of manganese dioxide has

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* Roman numerals refer to corresponding sections of the experimental part.

been described on p. 1626, and it is shown that the reduction is a surface reaction (VII). If manganous sulphate solution is added with the oxalic acid to the manganese dioxide, the latter is again rapidly dissolved to a clear yellow solution, but the oxidising power is not halved, being only slightly reduced. (It subsequently diminishes owing to the slow decomposition of the complex.) Hence, more tervalent manganese is being formed than corresponds to the reduction of all the manganese dioxide by oxalic acid. This must be due to the occurrence of the reaction (cf. Launer)

$$\mathrm{Mn^{\cdot\cdot\cdot\cdot} + Mn^{\cdot\cdot} \longrightarrow 2Mn^{\cdot\cdot\cdot}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

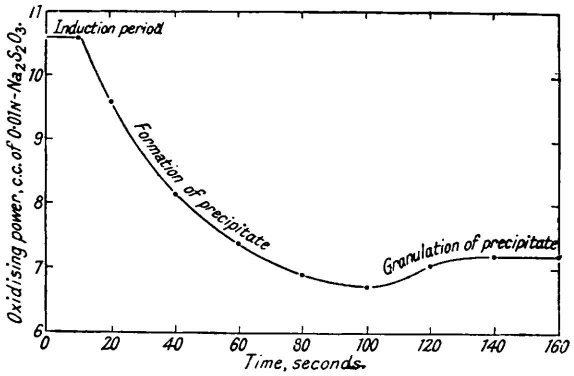
in addition to the reduction by the oxalic acid:

$$\mathrm{Mn^{\cdot\cdot\cdot\cdot} + C_2O_4'' \longrightarrow Mn^{\cdot\cdot} + 2CO_2} \quad . \; . \; . \; . \; . \; . \; . \quad (5)^*$$

Thus the manganese dioxide is reacting in two ways: (i) according to equation (4), producing no change in the oxidising power, and (ii), according to (5), causing a reduction in oxidising power. Reaction (4) does not take place unless the manganic ions are removed as complex ions by the oxalic acid. By varying the concentration of the manganous sulphate solution added, the rate of reaction (4) could be modified (VIII, X).

The simultaneous occurrence of these two reactions provides another means of showing that reaction (5) is a surface reaction. Various amounts of manganese dioxide were converted into tervalent manganese in solutions containing different concentrations of oxalic acid and the same concentration of manganous ions. The oxidising power was reduced to the same fraction of its original value by oxalic acid present in concentrations varying over. an eight-fold range. A similar test applied to the reaction of the manganese dioxide with manganous ions did not show that the reaction was a surface one (IX). On the assumption that the reaction (4) is homogeneous and that (5) is a surface change, a relation can be deduced between the change in the oxidising power of the mixture and the concentration of the manganous sulphate, independent of the oxalic acid concentration. This relation was in reasonable agreement with the experimental results (X).

FIG. 2.



Further evidence for the reaction (4). When potassium fluoride is added to a mixture of oxalic acid and manganese dioxide, preventing the formation of the manganioxalate complex (see p. 1625), the oxidising power of the mixture falls to exactly half that of the original manganese dioxide. If the oxalic acid is omitted, and manganous sulphate added instead, the manganese dioxide is again dissolved, but the oxidising power remains unchanged. The fact that this reaction does not occur except in acid solution suggests that it involves quadrivalent manganese *ions*.

There is thus no doubt that the reaction (4) does in fact occur, and that the equilibrium $\mathrm{Mn^{\cdot\cdot\cdot\cdot} + Mn^{\cdot\cdot} \rightleftharpoons 2Mn^{\cdot\cdot\cdot}}$ can be moved to the right by either oxalate or fluoride ions, both of which reduce the $\mathrm{Mn^{\cdot\cdot\cdot}}$ concentration through the formation of a complex ion.

(3) *The Decomposition of the Manganioxalate Complex.*—It has now been shown that the yellow solution formed from potassium permanganate, manganous sulphate, and oxalic acid solutions contains tervalent manganese in the form of a complex oxalate. This slowly decomposes, becoming colourless, as the manganic part oxidises the oxalate part.

Lidwell and Bell (*loc. cit.*) ascribed the formula $\mathrm{Mn(C_2O_4)_3'''}$ to the complex ion. They found that the salt $\mathrm{K_3Mn^{III}(C_2O_4)_3}$ (Kehrmann, *Ber.*, 1887, **20**, 1594) decomposed

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* In this equation the reagents are represented as ions without prejudice as to the precise ionic or molecular form in which they react.

in acid solutions at a rate similar to that of the yellow complex. We prepared the trihydrate according to Cartledge and Ericks (*J. Amer. Chem. Soc.*, 1936, **58**, 2061).

Fessenden and Redman (*ibid.*, 1935, **57**, 2246) assume the existence of the ion $Mn(C_2O_4)_2{}'$, also postulated by Launer (see p. 1625), and regard it as very unstable. Cartledge and Ericks (*loc. cit.*) prepared the salt K $[Mn^{III}(C_2O_4)_2(H_2O)_2]$, and found the value $3{\cdot}8 \times 10^{-3}$ at 0° for the constant of the equilibrium $[Mn(C_2O_4)_3]''' + 2H_2O \rightleftharpoons [Mn(C_2O_4)_2(H_2O)_2]' + C_2O_4''$, attributing a red colour to the tervalent and a yellow colour to the univalent ion, and thus accounting for the colour change from cherry-red to golden-yellow undergone by concentrated solutions of $K_3Mn(C_2O_4)_3$ on dilution. This also explains why a dilute solution of the salt becomes pink when added to a solution in which the oxalate-ion concentration is greater than about 0·003M.

In agreement with this, we found that in a solution in which $[H^{\cdot}] = 0{\cdot}01$M, $[H_2C_2O_4] = 0{\cdot}008$M, and therefore $[C_2O_4''] = 0{\cdot}0001$M, the solution was yellow; but that when these concentrations were respectively 0·0003, 0·01, and 0·003M, the solution was just pink. These colour changes occur both with solutions of the salt $K_3Mn(C_2O_4)_3$ and with those obtained from manganese dioxide and oxalic acid. This strongly suggests that the latter solution, when yellow, contains the ion $[Mn(C_2O_4)_2(H_2O)_2]'$, and not the ion $[Mn(C_2O_4)_3]'''$, as suggested by Lidwell and Bell. They ascribed the colour change from purple to yellow occurring on acidification of a solution of the salt $K_3Mn(C_2O_4)_3$ to the formation of a neutral molecule $Mn(HC_2O_4)_3$, but it is clear from the work of Cartledge and Ericks that the effect of hydrogen ions is to shift the above equilibrium to the right by reducing the oxalate-ion concentration.

The study of the decomposition of the yellow solution obtained from the manganese dioxide and oxalic acid is complicated by the presence in unknown amount of ions other than the manganioxalate ion. We found it more convenient to use the yellow solutions obtained from potassium manganioxalate for the quantitative study of the decomposition of the complex ion. The behaviour of the yellow solutions obtained in the two different ways was shown to be the same (XII).

The decomposition of solutions of potassium manganioxalate. Solutions of potassium manganioxalate decompose spontaneously, becoming colourless owing to the reduction of the tervalent manganese by the oxalate part of the salt. The rates of loss of oxidising power of solutions of this salt have been measured (XI). The decomposition products, particularly oxalic acid, materially affect the rates, so measurements were made in media containing sufficient oxalic acid and hydrogen ion to reduce variations in these products to negligible proportions. Further, only the initial rates were measured. Since the reaction is unimolecular with respect to oxidising power provided other concentrations remain constant, the initial rates were best obtained from the initial slopes of the log (oxidising power)–time graphs, and are represented below by k (min.$^{-1}$) (see Figs. 3, 3a, and 4).

Results.—The effect of concentration of the complex. The following table shows the effect of concentration of the salt on its rate of decomposition in various media.

Expt.	Medium.	Colour.	Initial concn. (g.-equivs. of Mn^{IV} in 10^6 c.c.).	Rate, k (min.$^{-1}$).
Experiments with solutions made from potassium manganioxalate.				
268	N/50-Sulphuric acid	Pale yellow	0·035	0·090
266	,, ,,	Brownish-red	0·70	0·017
272	M/50-Oxalic acid + M/100-manganese sulphate	Brownish-yellow	0·20	0·022
273		Cherry-red	1·40	0·016
279	N/1000-Sulphuric acid	Pale yellow	0·01	0·046
278	,, ,,	Brownish-yellow	0·084	0·013
280	,, ,,	Cherry-red	0·84	0·008
299	N/100-Sulphuric acid + M/1000-oxalic acid	Yellow	0·005	0·07
289		,,	0·011	0·07
300		,,	0·021	0·07
Experiments with solutions made from manganese dioxide and oxalic acid.				
98	*ca.* M/25-Oxalic acid	Yellow	0·12	0·011
105		,,	0·014	0·012
133	*ca.* M/50-Oxalic acid	,,	0·009	0·004
128		,,	0·016	0·006
134		,,	0·031	0·005

It is clear that the more concentrated solutions, which were pink, decompose more slowly than the more dilute, yellow solutions, which contained the ion $[\mathrm{Mn(C_2O_4)_2(H_2O)_2}]'$ (see p. 1628). As we were interested in the decomposition of the yellow solutions produced from manganese dioxide and oxalic acid, we confined the last three sets of experiments to solutions of low manganioxalate concentration in media of such oxalate-ion concentration that they were yellow.

FIG. 3.

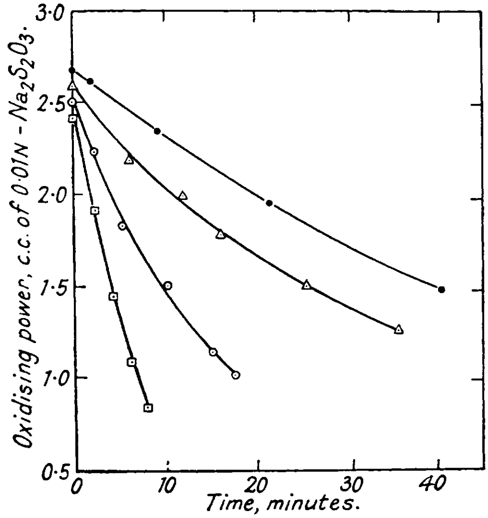


FIG. 3A.

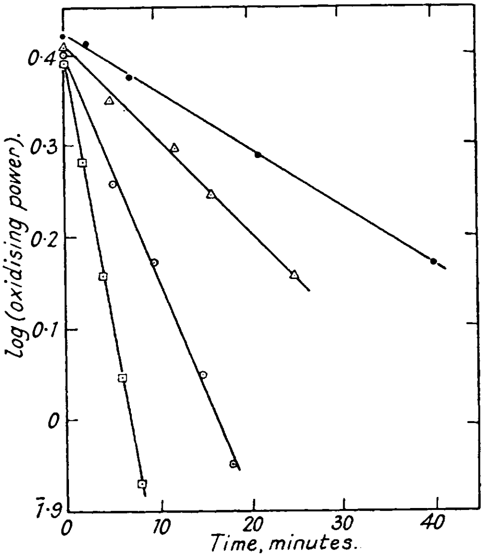
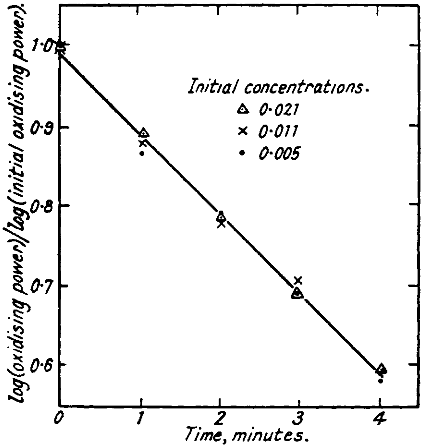


FIG. 4.



In solutions in which the salt is wholly in the yellow form, the decomposition is unimolecular with respect to oxidising power: $R = k[C]$, where C represents the complex manganioxalate ion. (It is assumed that the tervalent manganese is present almost entirely as the complex ion.)

The effect of concentration of hydrogen ion and of oxalic acid. The rate of decomposition of the complex salt is raised by an increase in the hydrogen-ion concentration, and lowered by an increase in the oxalic-acid concentration. The effect of oxalic acid is complex, and is best understood by reference to Figs. 5—7. The decomposition is greatly retarded by traces of oxalic acid (Fig. 5). At constant hydrogen-ion concentration, the graphs of

k against $1/[H_2C_2O_4]$ are linear (Fig. 6). Thus $k = a/[H_2C_2O_4] + b$, but a and b are functions of $[H^{\cdot}]$. In solutions of the same oxalic acid molecule concentration, the rate is directly proportional to the hydrogen-ion concentration (Fig. 7). These facts are expressed by the equation $k = [H^{\cdot}](A/[H_2C_2O_4] + B)$. From the graphs it is found that $A = 1{\cdot}13 \times 10^{-3}$ and $B = 1{\cdot}67$.

The equation was tested by plotting k against $[H^{\cdot}]/[H_2C_2O_4] + [H^{\cdot}]B/A$ (Fig. 8). It seems therefore that the reaction rate is satisfactorily expressed by the equation

$$R = [C][H^{\cdot}](1{\cdot}13 \times 10^{-3}/[H_2C_2O_4] + 1{\cdot}67)$$

The graphs show that the rate ceases to be proportional to the hydrogen-ion concentration at high values of the latter, the rates then being too high. This may be due to the assumptions made in calculating the ionic concentrations, *viz.*, that Ostwald's dilution law holds, that the second ionisation of the oxalic acid can be neglected, and that the sulphuric acid was completely dissociated.

FIG. 5.

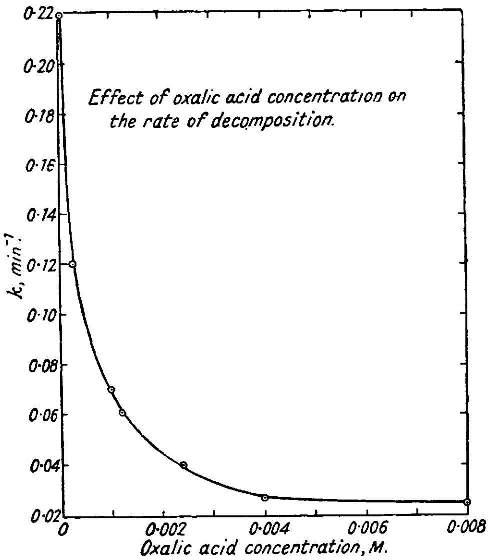
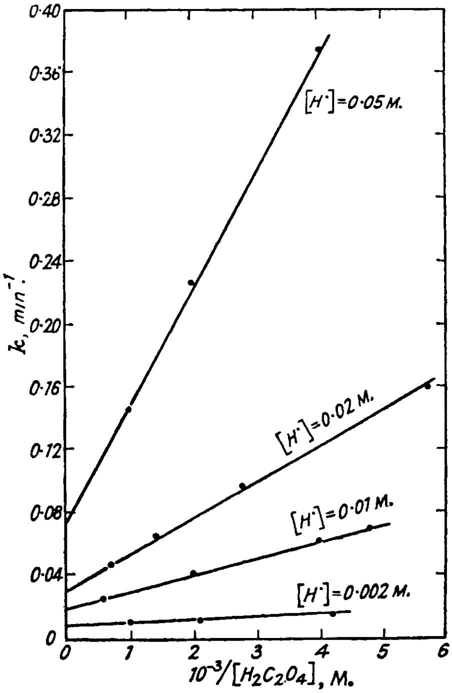


FIG. 6.



The effect of manganous-ion concentration on the rate of decomposition is complex; the manganioxalate solutions formed by the two methods are similarly affected. The rates of decomposition are unaffected by small concentrations of manganous ion in dilute or concentrated acid solutions containing no oxalic acid, but in media containing only a little oxalic acid (M/2000) the rate is greatly reduced by small concentrations of manganous ion (M/1000). This will be the subject of further investigation.

Suggested Mechanism for the Decomposition of the Manganioxalate Ion.—It is assumed that the complex ion $[(Mn^{III}(C_2O_4)_2(H_2O)_2]'$ is dissociated by hydrogen ions giving rise to free $Mn^{\cdot\cdot\cdot}$ ions (6), and that the decomposing solution contains small and constant concentrations of the ions $Mn^{\cdot\cdot\cdot\cdot}$ and $Mn^{\cdot\cdot\cdot}$. The rate-determining steps are the reductions of these two ions by oxalic acid.

$$H^{\cdot} + \{Mn^{III}(C_2O_4)_2(H_2O)_2\}' \xrightarrow{k_1} Mn^{\cdot\cdot\cdot} + HC_2O_4' + C_2O_4'' + 2H_2O \quad . \quad (6)$$

$$2Mn^{\cdot\cdot\cdot} \xrightarrow{k_2} Mn^{\cdot\cdot} + Mn^{\cdot\cdot\cdot\cdot} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

$$Mn^{\cdot\cdot\cdot\cdot} + H_2C_2O_4 \xrightarrow{k_3} Mn^{\cdot\cdot\cdot} + 2H^{\cdot} + CO_2' + CO_2 \quad . \; . \; . \; . \quad (8)$$

(followed by $Mn^{\cdot\cdot\cdot\cdot} + CO_2' \longrightarrow Mn^{\cdot\cdot\cdot} + CO_2$) . . . . . . (8*a*)

$$2Mn^{\cdot\cdot\cdot} + H_2C_2O_4 \xrightarrow{k_4} 2Mn^{\cdot\cdot} + 2H^{\cdot} + 2CO_2 \quad (9)$$

Then we have

$$d[Mn^{\cdot\cdot\cdot}]/dt = k_1[H^{\cdot}][C] + k_3[Mn^{\cdot\cdot\cdot\cdot}][H_2C_2O_4] - k_2[Mn^{\cdot\cdot\cdot}]^2 - k_4[Mn^{\cdot\cdot\cdot}]^2[H_2C_2O_4]$$

$$d[Mn^{\cdot\cdot\cdot\cdot}]/dt = k_2[Mn^{\cdot\cdot\cdot}]^2 - k_3[Mn^{\cdot\cdot\cdot\cdot}][H_2C_2O_4]$$

Since $[Mn^{\cdot\cdot\cdot}]$ and $[Mn^{\cdot\cdot\cdot\cdot}]$ are assumed to be constant,

$$[Mn^{\cdot\cdot\cdot\cdot}] = k_2[Mn^{\cdot\cdot\cdot}]^2/k_3[H_2C_2O_4] \text{ and } [Mn^{\cdot\cdot\cdot}]^2 = k_1[H^{\cdot}][C]/k_4[H_2C_2O_4]$$

The rate of loss of oxidising power is given by

$$R = k_3[Mn^{\cdot\cdot\cdot\cdot}][H_2C_2O_4] + k_4[Mn^{\cdot\cdot\cdot}]^2[H_2C_2O_4]$$

whence $$R = k_1k_2[H^{\cdot}][C]/k_4[H_2C_2O_4] + k_1[H^{\cdot}][C]$$

or $$R = [C][H^{\cdot}](k_1k_2/k_4[H_2C_2O_4] + k_1)$$

FIG. 7.

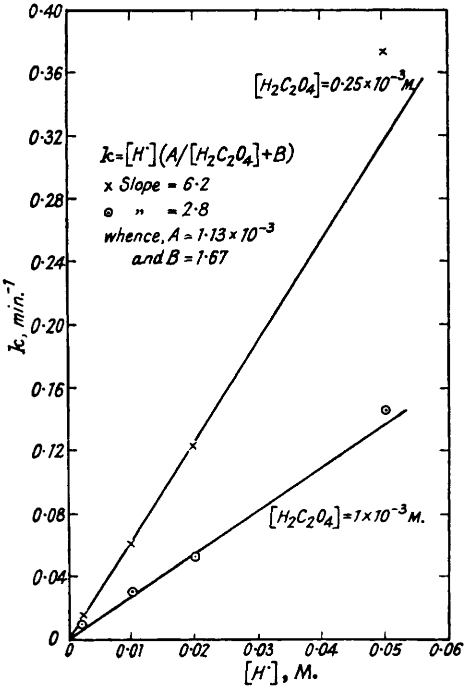
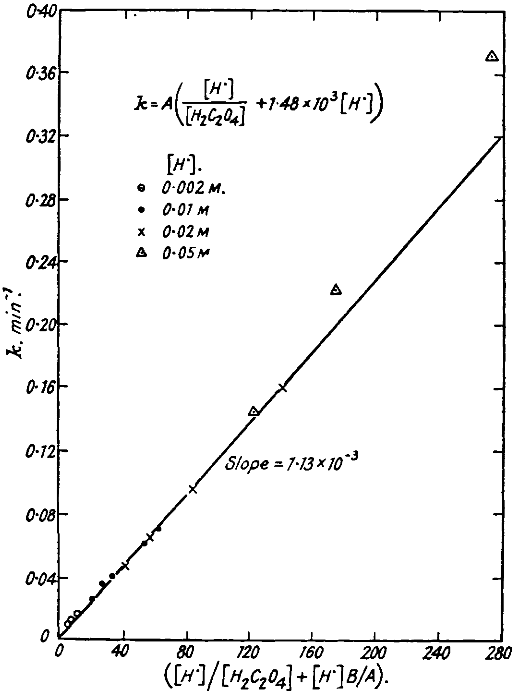


FIG. 8.



Reaction (7) has been shown to be reversible [cf. (4)], but in media containing initially no manganous ions, the reverse change can be ignored in calculations of the initial rates. However, the mechanism could be modified at this point in order to include the effect of manganous-ion concentration, which has been referred to above.

By comparison with the empirical equation for the rates of reaction, it is found that the rate constant for the decomposition of the complex ion, k_1, is 1·67 l. g.-mol.$^{-1}$ min.$^{-1}$. Values for k_2, k_3, and k_4 cannot be obtained, but $k_2/k_4 = 0{\cdot}68 \times 10^{-3}$. Thus the rates of reactions (7) and (9) are equal in a solution of oxalic acid molecule concentration of $0{\cdot}68 \times 10^{-3}$M. (This was approximately the case in Experiment 307.)

EXPERIMENTAL.

The experiments were all performed at 16° ± 1°.

(I) *Expt.* 4.—10 C.c. each of 0·0018M-potassium permanganate, 0·009M-manganous sulphate, and 0·0178M-sulphuric acid were mixed, and after time *t*, 10 c.c. of M/50-oxalic acid were added. After 2 minutes the reaction was stopped by adding potassium iodide solution, and the liberated iodine titrated with N/100-thiosulphate:

t, mins.	0	2	4	6	8
N/100-$Na_2S_2O_3$, c.c.	6·14	4·84	4·10	3·84	3·86

(II) *Expts.* 45—53.—We wished to know whether the precipitate produced from potassium permanganate and manganous sulphate contained ter- or quadri-valent manganese oxide. Meyer and Nerlich observed that the acid hydrolysis of manganic salts leads to the formation of manganese dioxide and manganous salt, and that alkalis precipitate manganic hydroxide from a manganic salt solution. These observations were verified as follows: Green manganic sulphate crystals were prepared from potassium permanganate and sulphuric acid (Franke, *J. pr. Chem.*, 1887, **36**, 3), and a portion added to dilute sulphuric acid; a light brown precipitate was formed, and after addition of excess of aqueous ammonia, this was filtered off, and hydrogen sulphide passed into the filtrate, a pink precipitate of manganous sulphide being formed. Hence, some manganous sulphate had been produced by the acid hydrolysis of the manganic sulphate: $Mn_2(SO_4)_3 + 2H_2O \longrightarrow MnO_2 + MnSO_4 + 2H_2SO_4$.

Another portion of the manganic sulphate was added directly to dilute aqueous ammonia, and after removal of the light brown precipitate, the filtrate gave no precipitate with hydrogen sulphide, so the precipitate must have been manganic hydroxide. Hence, in acid solution, manganic sulphate hydrolyses according to the above equation, but this does not occur in alkaline solution.

If manganous sulphate and excess potassium permanganate are mixed in acid solution, the brown precipitate filtered off, and the filtrate made alkaline with ammonia, the solution contains no manganous ions, for it gives no precipitate with hydrogen sulphide. If the brown precipitate had been manganic hydroxide, it would have undergone acid hydrolysis to manganese dioxide and manganous sulphate, but since manganous ions were absent, it follows that the precipitate is manganese dioxide.

(III) *Expts.* 36, 37, 47.—Mn_2O_3 and MnO_2, prepared by methods recorded by Mellor ("A Comprehensive Treatise, etc.," Vol. 12, pp. 228, 240), reacted rapidly with oxalic acid to form yellow solutions. The two oxides obtained from manganic sulphate (II) behaved in the same manner.

(IV) *Expt.* 60.—Several mixtures containing 10 c.c. each of 0·00182M-potassium permanganate and 0·00546M-manganous sulphate solutions were left to precipitate completely (about 10 mins.); 10 c.c. of M/50-oxalic acid were then added, and after various time intervals, *t*, the reactions were stopped by adding acidified potassium iodide solution. The residual oxidising power was then found by titration with N/100-thiosulphate:

t, secs.	0	10	30	50	70	90	110
N/100-$Na_2S_2O_3$, c.c.	10·0	6·96	5·65	5·25	4·95	4·95	5·00

Similar experiments were performed with different quantities of manganese dioxide, and in all cases the initial rapid reduction ceased when the oxidising power of the solution had fallen to half its original value.

(V) The reaction between potassium permanganate and manganous sulphate was followed by utilising the fact that oxalic acid is oxidised much faster by manganese dioxide than by potassium permanganate. A standard quantity of oxalic acid was added to the reacting mixture after time *t*, and left for a suitable period (about 10 secs.) to remove the manganese dioxide formed by the reaction. During this time the amount of permanganate reduced was very small. Potassium iodide solution was then added, and the free iodine titrated with thiosulphate. A titre is thus obtained which is an index of the amount of permanganate undecomposed.

Expt. 233.—*Effect of acid concentration on the rate of reaction between potassium permanganate and manganous sulphate.*

$KMnO_4$ = 0·004M; $MnSO_4$ = 0·006M.

Acidity, N	0	0·001	0·005	0·010	0·015	no reaction
$KMnO_4$ undecomposed after 60 secs., c.c. of N/100	5·7	6·3	7·2	8·4	9·3	10·6

(VI) *Expt.* 239.—The course of the above reaction with time was then followed in the presence of 0·005N-sulphuric acid (see Fig. 2):

t, secs.	0	10	20	40	60	80	100	120	140	160
$KMnO_4$ undecomposed after 60 secs., c.c. of N/100	10·68	10·61	9·60	8·14	7·34	6·87	6·69	7·06	7·22	7·14

The granulation of the precipitate, which occurs after about 100 secs., has the effect of increasing the titre, for the granular manganese dioxide reacts more slowly with the oxalic acid than does the fresh precipitate.

Expt. 221.—The induction period could be eliminated as follows. Two reaction mixtures, *A* and *B*, were left to produce manganese dioxide for 10 mins. Two portions of permanganate, *X* and *Y*, were then treated as follows:

	Time, secs.			Iodine liberated,
	0.	5.	15.	c.c. of N/100.
X.	Equiv. vol. of $MnSO_4$ added	Oxalic acid and reaction mixture *A* added	Excess KI added	18·17
Y.	$MnSO_4$ as above and reaction mixture *B* added	Oxalic acid added	Ditto	16·74

The results show that more manganese dioxide was produced in *Y*, in which manganese dioxide was already present, than in *X*. A small effect was also obtained by the addition of finely powdered glass wool:

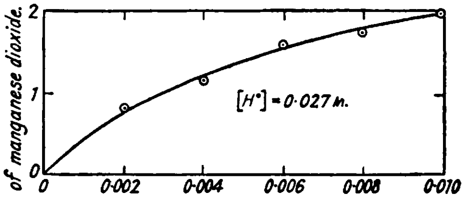
		Titre, c.c.
Expt. 223.—*X*.	Glass wool added with the oxalic acid	10·58
Y.	,, ,, ,, $MnSO_4$	10·06

(VII) *Expts.* 81, 86.—The initial rates of reaction between manganese dioxide and various concentrations of oxalic acid in very dilute acid solutions were found as in the above experiments. The rate at first increased with the oxalic acid concentration, but became independent of it in less dilute solutions (see Figs. 9 and 10).

Expts. 61, 62, 87.—Solutions containing severally half and twice the concentrations of those used in Expt. 60 were then used to precipitate manganese dioxide. The same concentration of oxalic acid was added. The amount of decomposition in the first 10 secs. was found to be proportional to the quantity of manganese dioxide present. Since the acid produced in the reaction by which the manganese dioxide is formed is also proportional to the amount of the latter, it was possible that this was responsible for the changes in rate. Other mixtures were therefore made, and the resulting manganese dioxide filtered off and washed. The initial rates of reaction with oxalic acid were, however, still proportional to the amount of manganese dioxide.

(VIII) *Expt.* 211.—Reaction mixtures were prepared from equivalent solutions of potassium permanganate (2M/500) and manganous sulphate (3M/500). The oxidising power of the manganese dioxide in one reaction mixture was 10·6 c.c. as measured by the volume of N/100-thiosulphate required for the iodine liberated. The reaction was started by addition of 40 c.c. of a solution of oxalic acid and manganous sulphate of such concentrations that the resulting medium was M/10 in oxalic acid and M/100—M/1000 in manganese sulphate. It was stopped after 10 secs. by addition of potassium iodide solution.

FIG. 9.



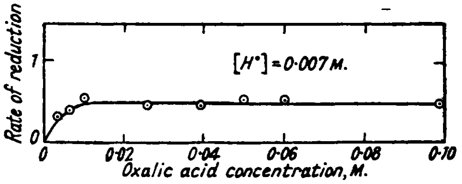


FIG. 10.

$MnSO_4$, M	0	1/1000	1/500	1/250	1/200	1/150	1/100
Oxidising power after 10 secs., in c.c. of N/100-$Na_2S_2O_3$	4·38	6·03	6·80	7·68	7·76	7·98	8·66

Thus in the more concentrated manganous sulphate solutions the reaction (4) predominates over the reduction (5) (see p. 1627). (The reduction of the oxidising power below ½ × 10·6, *viz.*, to 4·38 in the first experiment, is due to decomposition of the manganioxalate.)

(IX) *Expts.* 225—228 (see p. 1627).

MnO_2, mols. × 10^{-4}.	Vol. of solution, c.c.	[Oxalic acid.]	Oxidising power after 10 secs., c.c. of N/100-$Na_2S_2O_3$
0·25	25	M/5	4·10
0·5	50	M/10	8·44 = 2 × 4·22
1·0	100	M/20	16·17 = 2 × 8·36
2·0	200	M/40	33·95 = 2 × 16·97

The figures in the last column have been corrected for the decomposition of the complex; this was also done in the following experiment.

Expt. 224.

MnO_2, mols. × 10^{-4}.	Vol. of solution, c.c.	$[Mn^{\cdot\cdot}]$.	Oxidising power after 10 secs., c.c. of N/100-$Na_2S_2O_3$.
0·5	50	M/200	8·44
1·0	100	M/400	15·20 = 2 × 7·60

The concentration of oxalic acid was M/10 in both these experiments. In the solution of smaller manganous-ion concentration, reaction (4) is diminished.

(X) *Expts.* 207—210, 241—242, 245—247.—*Further measurements on the dissolution of manganese dioxide by mixed solutions of oxalic acid and manganous sulphate, and the deduction of an expression for the change in oxidising power so produced.* The only reaction in which reduction occurs is the surface reaction between the manganese dioxide and the oxalic acid (5). Provided there is something to remove the $Mn^{\cdot\cdot\cdot\cdot}$ ions, the following change (probably also a surface reaction) can also occur: $2MnO_2 + 8H^{\cdot} \longrightarrow 2Mn^{\cdot\cdot\cdot\cdot} + 4H_2O$. The reaction of the oxalic acid with $Mn^{\cdot\cdot\cdot\cdot}$ ions is assumed to be negligible compared with its reaction with solid manganese dioxide. In the presence of $Mn^{\cdot\cdot}$ ions, the reaction (4) occurs, producing tervalent manganese (which forms the oxalate complex) without loss of oxidising power. Suppose we start with a mass M of surface of manganese dioxide, which changes during the experiment through values of m to 0, taking a time t to do so. When an experiment begins, the two reactions (4) and (5) set in. Let the constant of reaction (5) be P, *i.e.*, the loss of oxidising power per unit mass of surface per second. The rate of reaction (4) is assumed to be determined by the manganous-ion concentration (the concentration of $Mn^{\cdot\cdot\cdot\cdot}$ being assumed to be small and constant), and is equal therefore to $k[Mn^{\cdot\cdot}]$, where k is a constant. If x_0 represents the oxidising power of the original manganese dioxide, and x the value to which it is reduced when all the dioxide has been consumed by the mixed oxalic acid–manganous sulphate solution, the oxidising power conserved by reaction (4) is measured by $(x - \frac{1}{2}x_0)$. Hence

$$k[Mn^{\cdot\cdot}]t = x - \tfrac{1}{2}x_0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

The rate of the reduction by oxalic acid (5) is affected by the hydrogen-ion concentration, but Expt. 87 showed that the effect was not appreciable over the range used, so the loss of oxidising power occurring in time t is $\int_0^M \int_0^t P.dt.dm = PMt$, and this is measured by $(x_0 - x)$. Hence

$$PMt = x_0 - x \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

From (10) and (11) it follows that $[Mn^{\cdot\cdot}]/(x - \frac{1}{2}x_0) = 2[Mn^{\cdot\cdot}]/x_0 + c$ where c is a constant. These equations have been tested and the results are shown in Fig. 11.

The experiments were performed as described under (VIII), three different initial quantities of manganese dioxide being used. The oxalic acid concentration was M/25, and that of the manganous sulphate, $[Mn^{\cdot\cdot}]$, was varied; x_0 and x are given in terms of c.c. of N/100-thiosulphate.

$10^3[Mn^{\cdot\cdot}]$.	x_0.	x.	$\frac{10^3[Mn^{\cdot\cdot}]}{x-\frac{1}{2}x_0}$.	$10^3[Mn^{\cdot\cdot}]$.	x_0.	x.	$\frac{10^3[Mn^{\cdot\cdot}]}{x-\frac{1}{2}x_0}$.	$10^3[Mn^{\cdot\cdot}]$.	x_0.	x.	$\frac{10^3[Mn^{\cdot\cdot}]}{x-\frac{1}{2}x_0}$.
2	21·6	14·35	0·56	2	11·1	7·48	1·06	1	5·4	3·61	1·10
4	,,	15·64	0·82	4	,,	8·21	1·50	2	,,	3·96	1·59
5	,,	16·22	0·92	5	,,	8·28	1·83	4	,,	4·30	2·50
6·7	,,	17·10	1·06	6·7	,,	8·74	2·10	5	,,	4·33	3·00
								6·7	,,	4·57	3·58

$10^3[Mn^{\cdot\cdot}]$.	x_0.	x.	$x - \frac{1}{2}x_0$.	t, secs.	$t \times [Mn^{\cdot\cdot}] \times 10^3$.
3	10·7	18·14	2·79	$4\frac{1}{2}$	13·5
1	,,	6·58	1·23	$4\frac{3}{4}$	4·7
3	21·4	14·91	4·21	$5\frac{1}{2}$	16·5
1	,,	12·23	1·53	$6\frac{1}{2}$	6·5
3	5·35	4·00	1·30	$3\frac{1}{4}$	9·7
1	,,	3·60	0·90	$3\frac{1}{2}$	3·5

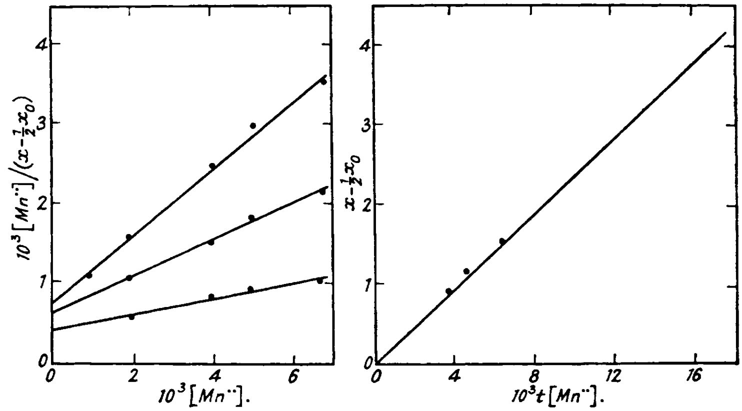
The slopes of the graphs should be numerically equal to $2/x_0$:

Slope	0·100	0·25	0·43
$2/x_0$	0·093	0·19	0·37

The agreement could not be expected to be good, as the theory neglects a number of factors, *e.g.*, the decomposition of the complex during the time t. Further, it is not possible to measure the time to an accuracy of more than about 10%, as it is difficult to decide exactly when all the manganese dioxide has reacted.

(XI) *The Decomposition of Potassium Manganioxalate.*—The salt was prepared by Cartledge and Ericks's method (*loc. cit.*) [Found: Mn, 11·0. Calc. for $K_3Mn(C_2O_4)_3,3H_2O$: Mn, 11·2%]. A weighed quantity of the salt was dissolved in a large volume of the solvent, dissolution being complete in a few seconds; a measured volume was removed at known intervals, the reaction stopped by addition of a large excess of acidified potassium iodide solution, and the iodine liberated titrated with N/100-thiosulphate. (If only a small excess of iodide is used, iodine is liberated so slowly as to vitiate the titrations. Also, in certain experiments, after all the iodine had been removed by the thiosulphate, more iodine appeared, in some cases, after only a few seconds; the rate of re-formation of iodine was greater in media of high oxalic acid, manganous sulphate, and potassium iodide concentration, and in solutions in which the decomposition of the manganioxalate had proceeded for some time. Further experiments showed that this was due to oxidation of hydriodic acid by oxalic acid, catalysed by manganese. The phenomena are being further investigated.)

FIG. 11.



In most experiments, 0·1 g. of the salt was dissolved in 2 l. of solvent, and 250 c.c. removed each time for titration. The following details for Expt. 246 are typical of the method used for preparing the medium. A solution was required of hydrogen-ion concentration = 0·01M and oxalic acid molecule concentration = 0·0005M. Let x be the over-all concentration of the oxalic acid; then $[HC_2O_4'] + 0{\cdot}0005 = x$, and $0{\cdot}01 \times [HC_2O_4']/0{\cdot}0005 = 0{\cdot}038$, since 0·038 is the constant for the first dissociation of oxalic acid. Whence $[HC_2O_4'] = 0{\cdot}0019$, and $x = 0{\cdot}0024$M. The hydrogen-ion concentration in 0·0024M-oxalic acid is therefore 0·0019M, and the additional $[H^{\cdot}]$ required is 0·0081M, so the solution was prepared by mixing 16·2 c.c. of N-sulphuric acid and 24 c.c. of M/5-oxalic acid and diluting them to 2 l. with distilled water.

About 80 experiments of this type were performed, and some of the results are shown in the following table. In all these experiments the initial concentration of the salt was 1 g.-equivalent per 10,000 l.

Expt. No.	$[H^{\cdot}]$.	$\frac{10^{-3}}{[H_2C_2O_4]}$.	k, min.$^{-1}$.	$\frac{[H^{\cdot}]}{[H_2C_2O_4]} + 1{\cdot}48 \times 10^3[H^{\cdot}]$.
311	0·002	1·03	0·009	5·1
312	,,	2·08	0·011	7·2
313	,,	4·16	0·015	11·4
289	0·01	4·8	0·07	62·8
291	,,	1·2	0·035	26·8
294	,,	0·6	0·025	20·8
345	,,	4·0	0·061	54·8
346	,,	2·0	0·040	34·8
307	0·02	1·4	0·064	57·6
308	,,	0·7	0·046	43·6
309	,,	2·8	0·096	85·6
310	,,	5·7	0·160	141·6
314	0·05	1·0	0·145	124·0
315	,,	2·0	0·225	174·0
306	,,	4·0	0·375	274·0

(XII) *Correlation between the Yellow Solutions from Potassium Manganioxalate and from Manganese Dioxide and Oxalic Acid.*—The following table gives the decomposition rates (*k*) in similar media : they are sufficiently alike to show that the two solutions contain the same decomposing substance.

Medium	M/500-H˙	M/50-H˙ + M/500-oxalic acid	M/100-H˙ + M/125-oxalic acid
		Values of *k*.	
Solution from $K_3Mn(C_2O_4)_3$	0·056	0·064	0·025
Solution from MnO_2 and oxalic acid	0·060	0·050	0·030

We are grateful to Mr. Henry Terrey, Mr. W. B. Newling, and Dr. E. A. Moelwyn-Hughes for advice, and to Mr. D. H. Burleigh for facilitating the performance of the work at Christ's Hospital.

CHRIST'S HOSPITAL, HORSHAM. [*Received, August* 13*th*, 1938.]