capacity of the solute, $\bar{c}_{p_2}$, the partial molal heat capacity of the solute, $\bar{c}_{p_1}$, the partial molal heat capacity of the solvent and the specific heat of the solution are given.

Tables and plots of the experimental data and tables of rounded values of Φ, $\bar{c}_{p_2}$, $\bar{c}_{p_1}$ and specific heat are given for the nitrates, chlorides, bromides, iodides and sulfates of sodium and potassium in aqueous solution from infinite dilution to 1.0 molal, and in some cases to 2.5 molal.

A theoretical equation for $\bar{c}_{p_2} - \bar{c}_{p_2}^{\circ}$ is derived on the basis of the Debye-Hückel theory of strong electrolytes in aqueous solution, and is compared with the experimentally determined values. ($\bar{c}_{p_2}^{\circ}$ refers to infinite dilution.)

The partial molal heat capacity of a given ion is shown to depend upon the charge, the size and the configuration of the ion. The partial molal heat capacities of ions are shown to be additive at infinite dilution.

The relation of the results obtained to hydration of ions and the temperature coefficient of the heat of solution of a strong electrolyte in a large amount of water is discussed.

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THE REDUCTION OF PERMANGANATE ION BY CHROMIC ION IN ACID SOLUTION

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The peculiar nature of the reduction of permanganate ion in acid solution has long interested chemists. As early as 1866 Harcourt and Esson[2] in their study of the reduction of permanganate by oxalic acid observed that the reaction was autocatalytic and catalyzed by manganous ion, and that in the presence of the latter excess of oxalic acid slowed down the rate of oxidation. They imputed the catalytic effect to the formation of manganese dioxide in solution.

In 1903 the study of the reduction by oxalic acid was again undertaken by Schilow,[3] who endeavored to show that the autocatalysis was due to the interaction between the permanganate and a trivalent manganic oxalate complex, the primary reduction product.

The same reaction was next studied by Skrabal,[4] who observed a period

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[1] This paper is constructed from a dissertation submitted by P. S. Roller in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Columbia University.

[2] Harcourt and Esson, *Phil. Mag.*, 201 (1866).

[3] Schilow, *Ber.*, **36**, 2735 (1903).

[4] Skrabal, *Z. anorg. Chem.*, **42**, 1 (1905).

of comparatively rapid reduction which he called the induction period. In this period the interaction between the manganous ion which had been liberated in the so-called incubation period and the permanganate ion *induced* a rapid oxidation of the oxalic acid. In the presence of excess manganous ion, this author discovered the reaction to be unimolecular. This result was imputed to the unimolecular decomposition of the trivalent manganic ion complex already postulated by Schilow.

The work of Krutweig[5] shows that the reduction of permanganate by tartaric acid is exactly similar to that by oxalic acid; that the same holds true for lactic and citric acids is indicated by the recent work of Dey and Dhar.[6]

The tendency of trivalent manganic ion to enter into a complex compound with anions, particularly of organic acids, has been frequently affirmed. Salts of the manganic complex with malonic and oxalic acids have recently been prepared by Meyer and Schramm,[7] the compositions of the complex acids being $H_3[Mn(C_3H_2O_4)_3]$ and $H_3[Mn(C_2O_4)_3]$.

In order to obtain a clearer understanding of the mechanism of the reduction of permanganate ion, it seemed desirable to study the reduction in a medium free from the disturbing influence of complex compound formation between the trivalent manganic ion and the reductant. Chromic ion, which reduces permanganate ion in acid solution slowly at 25°, was chosen because as a metallic cation it met this requirement of non-complex formation.

Method of Experiment and Analysis of Reaction Mixture.—Experiments were conducted at 25.1°. After coming to temperature potassium chrome alum solution was rapidly pipetted into a prepared permanganate solution, which contained sulfuric acid and any other reagents whose effect was to be determined. (In the experiments with "MnO_2 dissolved in H_2SO_4," the MnO_2 in solution was formed by allowing $MnSO_4$ to interact with the prepared $KMnO_4$ solution for sixteen minutes before the addition of the chrome alum.)

The chrome alum and the sulfuric acid were in excess. The concentrations were: MnO_4^-, 0.00144 *M*; Cr^{+++}, 0.0227 *M*; H_2SO_4, 2.92 *M*. All other concentrations are expressed as a ratio of these.

At definite intervals of time, 25 cc. of the reaction mixture was rapidly pipetted into a solution consisting of 60 cc. of 1.2 *M* sulfuric acid and 25 cc. of 0.5 *M* potassium bromide. Free bromine was instantly liberated by the MnO_4^-, and was extracted by carbon disulfide purified according to the method of Allery.[8] The $Cr_2O_7^{--}$ which had been formed in the reaction was titrated electrometrically with 0.01 *N* ferrous sulfate.

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[5] Krutweig, *Z. physik. Chem.*, **2**, 787 (1888).

[6] Dey and Dhar, *Z. Elektrochem.*, **32**, 586 (1926).

[7] Meyer and Schramm, *Z. anorg. allgem. Chem.*, **123**, 56 (1922); **157**, 190 (1926).

[8] Allery, *Bull. soc. chim.*, [2] **35**, 491 (1881).

To avoid reduction of the $Cr_2O_7^{--}$ by Br^- or by carbon disulfide, all analytical operations had to be carried out in the absence of sunlight.

The platinum electrode was steamed between titrations and occasionally immersed in cold cleaning mixture. All vessels were steamed before use.

The electrometric titration had to be completed with little delay and one might not run past the end-point, as the back titration was inaccurate.

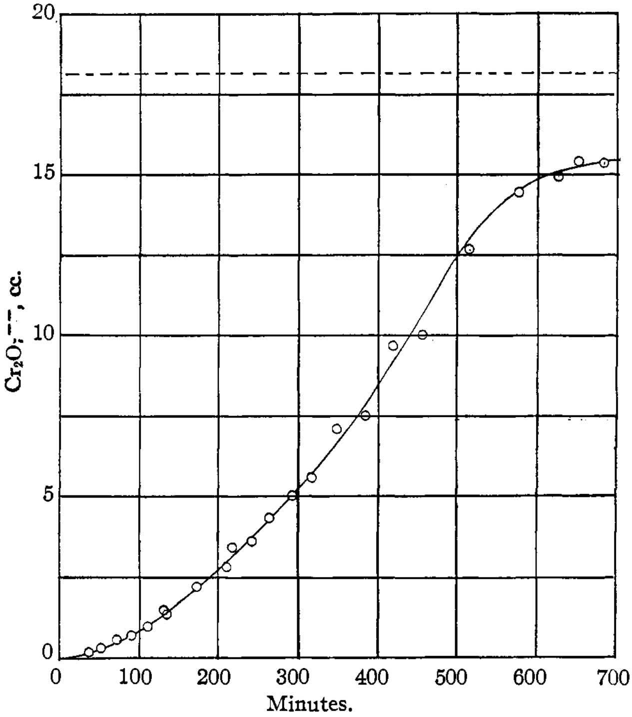

Fig. 1.—Reduction of MnO_4^- by Cr^{+++} in sulfuric acid solution at 25.1°.

The analysis of a series of prepared reaction mixtures showed the method to be accurate to ±0.05 cc. Check was frequently made on the analytical method.

It later occurred to the authors that it might be labor-saving to sweep out the dissolved bromine with air but this modification was not adopted in any of these experiments.

Reduction of MnO_4^- by Cr^{+++} in 2.92 *M* Sulfuric Acid Solution at 25.1°.—In Table I are given the results obtained in the direct reduction of MnO_4^- by Cr^{+++} ion. In the first column is the time in minutes from the instant that the chrome alum was added; in the second column is given the cc. of $Cr_2O_7^{--}$ (0.01 *N*) produced at the end of the corresponding time. The results of this table are plotted in Fig. 1.

TABLE I

REDUCTION OF MnO_4^- BY Cr^{+++} AT 25.1°

Initial concentrations: MnO_4^-, 0.00144 *M;* Cr^{+++}, 0.0227 *M;* H_2SO_4, 2.92 *M.*

Minutes	$Cr_2O_7^{--}$, cc.	Minutes	$Cr_2O_7^{--}$, cc.	Minutes	$Cr_2O_7^{--}$, cc.
30.92	0.18	217.3	3.40	444.7	9.94
51.42	.30	241.1	3.65	513.2	12.70
71.42	.59	263.8	4.30	575.2	14.40
89.70	.72	293.2	4.97	625.5	14.78
110.1	.98	318.0	5.56	649.5	15.38
130.0	1.46	348.9	7.10	683.2	15.28
134.2	1.30	383.0	7.49	712.4	15.35
173.2	2.23	418.4	9.68	∞	18.20
209.9	2.78				

From the figure it is seen that the initial slow oxidation is rapidly autocatalyzed to an almost linear rate of oxidation. This rate finally falls off rather abruptly to a slow retarded rate of reaction at a point several cc. below the maximum degree of oxidation. There is a close resemblance between the results here obtained and those of Schilow[3] on the oxidation of oxalic acid.

From the change in the magnitude of the initial rate of oxidation with a change in the MnO_4^- and Cr^{+++} concentrations, the order of this reaction may be determined. A number of points were determined in the neighborhood of the origin, a smooth curve was drawn and the time required for a given degree of oxidation read off from the curve. The results for different initial MnO_4^- and Cr^{+++} ion concentrations are shown in Table II.

TABLE II

ORDER OF THE MnO_4^-–Cr^{+++} REACTION IN SULFURIC ACID SOLUTION

Relative MnO_4^- concentration	1	2	1
Relative Cr^{+++} concentration	1	1	0.5
$Cr_2O_7^{--}$, cc.	Minutes	Minutes	Minutes
0.1	23	11	40
.2	36	18	70
.4	58	32	113
.6	77	44	148

It is seen from Table II that doubling the MnO_4^- concentration doubles the initial rate of oxidation, while decreasing the Cr^{+++} concentration by one-half produces a corresponding decrease in the initial rate. The order of the reaction between MnO_4^- and Cr^{+++} with the latter in excess is therefore bimolecular and, since the oxidation of the Cr^{+++} is presumably to the hexavalent state, the reaction may be represented by the following equation, in which the reduction of MnO_4^- is to the tetravalent Mn.

$$MnO_4^- + Cr^{+++} = CrO_4^{--} + Mn^{++++} \qquad (1)$$

The effect on the reaction between MnO_4^- and Cr^{+++} of changing the concentration of the sulfuric acid was determined in the same way. The results are shown in Table III.

TABLE III

EFFECT OF SULFURIC ACID ON THE MnO_4^--Cr^{+++} REACTION

Relative sulfuric acid concentration	1	0.5
$Cr_2O_7^{--}$, cc.	Minutes	Minutes
0.1	23	21
.2	36	30
.4	58	44
.6	77	54

From Table III it is seen that reducing the sulfuric acid concentration by one-half produces little effect on the rate of oxidation initially. Neglecting the purely ionic effects of changing the sulfuric acid concentration, this result is in accordance with the reaction expressed by Equation 1, since the hydrogen-ion concentration does not enter. As the oxidation proceeds, the effect of decreasing the acidity becomes more and more marked, resulting in an increase in the rate of oxidation. This is due to the strong effect of acid on the autocatalysis.

Oxidation of Cr^{+++} by Manganese Dioxide Dissolved in Sulfuric Acid.—As already indicated, by manganese dioxide dissolved in sulfuric acid we mean the mixtures obtained on adding Mn^{++} to MnO_4^- in acid solution. In the course of the oxidation of Cr^{+++} by MnO_4^- the products of the interaction between MnO_4^- and Mn^{++} will be present in solution. Since the oxidation rate of these products exceeds that of the permanganate itself, it was important, in order to obtain an insight into the nature of the permanganate reduction by chromic ion, to study their oxidation properties. To do this we measured the oxidation rate of mixtures of MnO_4^- and Mn^{++}, obtained by adding the latter to the former contained in sulfuric acid solution, such as would virtually be present in the course of the reduction of the MnO_4^- ion.

TABLE IV

OXIDATION OF Cr^{+++} BY MnO_2 DISSOLVED IN 2.92 M H_2SO_4

Ratio $Mn^{++}/MnO_4^- = 0.42$

Minutes	$Cr_2O_7^{--}$, cc.	Minutes	$Cr_2O_7^{--}$, cc.	Minutes	$Cr_2O_7^{--}$, cc.
5.30	0.26	104.8	5.71	225.8	13.30
15.50	.85	129.5	7.40	246.7	14.18
30.43	1.59	154.8	8.75	288.1	14.69
55.17	2.96	180.8	10.85	310.8	14.82
81.18	4.86	205.5	12.50	346.7	15.02

TABLE V

OXIDATION OF Cr^{+++} BY MnO_2 DISSOLVED IN 2.92 M H_2SO_4

Ratio $Mn^{++}/MnO_4^- = 2.11$

Minutes	$Cr_2O_7^{--}$, cc.	Minutes	$Cr_2O_7^{--}$, cc.	Minutes	$Cr_2O_7^{--}$, cc.
5.05	1.27	55.45	9.70	253.5	13.98
11.35	2.54	82.64	10.93	357.7	14.33
19.95	4.66	111.3	11.89	447.0	14.71
35.00	7.23	142.0	12.12	617.5	15.08

TABLE VI

OXIDATION OF Cr^{+++} BY MnO_2 DISSOLVED IN 2.92 M H_2SO_4

Ratio Mn^{++}/MnO_4^{-} = 4.22

Minutes	$Cr_2O_7^{--}$, cc.	Minutes	$Cr_2O_7^{--}$, cc.	Minutes	$Cr_2O_7^{--}$, cc.
5.38	2.04	42.88	7.28	195.1	12.58
10.60	3.57	81.47	9.54	268.6	13.81
20.27	5.58	111.9	11.20		

The results which were obtained for different ratios of Mn^{++} to MnO_4^{-} are shown in Tables IV, V and VI, and are also plotted in Fig. 2 as Curves A, B and C, respectively.

In Curves A, B and C of Fig. 2, where the ratios of Mn^{++} to MnO_4^{-} are 0.42, 2.11 and 4.22, respectively, the initial rate of oxidation of the Cr^{+++} is seen to increase with increase in the ratio. On the contrary, the extent of oxidation after a sufficient period of time is greater in inverse order. This is seen to be due to the fact that the initial rate of oxidation falls off more rapidly the higher the ratio of Mn^{++} to MnO_4^{-}. Indeed, at a ratio 0.42 the curve is linear up to 14 cc. of $Cr_2O_7^{--}$, and at a ratio of 2.11 it is linear up to 6 cc. of $Cr_2O_7^{--}$.

An interpretation of these results throws considerable light on the question of the relationship of MnO_4^{-} to its ions of lower valence and their relative oxidizing characteristics.

Interaction between MnO_4^{-} and the Mn^{++} which has been added leads to the formation in acid solution of the trivalent Mn^{+++} ion and the tetravalent Mn^{++++} ion. Since these oxidize Cr^{+++} more rapidly than MnO_4^{-} itself, the reason for the increase in the initial rate of oxidation with increase in the ratio (up to 4.22) is understood.

The presence of excess MnO_4^{-} accounts for the initial linear rate of oxidation shown in Curves A and B. In the course of the oxidation the excess MnO_4^{-} interacts rapidly with the Mn^{++} which has been liberated to regenerate the reactive Mn^{+++} and Mn^{++++} and, indeed, since the rate is linear, in practically the same proportions in which they had originally been present.

The proportion of Mn^{+++} and Mn^{++++} may be estimated from the degree of linearity of the Curves A and B. Considering the latter, where the ratio of Mn^{++} to MnO_4^{-} is 2.11, the linearity extends over a period of 6 cc. of $Cr_2O_7^{--}$. Since this corresponds to the excess MnO_4^{-}, we find that the fraction of the total MnO_4^{-} which has been unacted on by the Mn^{++} added is, since 18.2 cc. of $Cr_2O_7^{--}$ corresponds to the complete reduction of the MnO_4^{-} to Mn^{++}, $^{6}/_{18.2}$, or close to $^{1}/_{3}$.

Let x be the number of moles of Mn^{+++} which has been formed, and a the initial total number of moles of MnO_4^{-}. The ratio of Mn^{++} to MnO_4^{-} being 2.11, and $^{2}/_{3}$ of the total MnO_4^{-} having interacted, the concentration of the Mn^{++++} which has been formed is $(2.78\ a-x)$. Since 5 Mn^{+++} is formed per mole of MnO_4^- and 5 Mn^{++++} for every 2 moles of MnO_4^- which have interacted, the following equation which accounts for the loss of MnO_4^- holds true

$$\frac{1}{5}x + \frac{2}{5}(2.78\,a - x) = 0.67\,a \tag{2}$$

Solving this equation for x, we obtain $x = 2.20\,a$, $(2.78\,a - x) = 0.58\,a$. Consequently, in this solution the Mn^{+++} is present to the extent of 79%, the Mn^{++++} to the extent of 21%.

Grube and Huberich[9] have measured the equilibrium between Mn^{++}, Mn^{+++} and Mn^{++++} in sulfuric acid solution. Mn^{+++} dissociates into Mn^{++++} and Mn^{++} according to the following equation

$$2\,Mn^{+++} = Mn^{++++} + Mn^{++} \tag{3}$$

The degree of dissociation is found to be augmented by a decrease in acidity due to the hydrolysis of the Mn^{++++} to MnO_3^{--}. Extrapolation from the results of these authors shows that at 2.92 M sulfuric acid the dissociation should be perhaps 80%. In the presence of MnO_4^- it should indeed be greater.

The preponderance of Mn^{+++} which we have shown to be present indicates that the interaction between MnO_4^- and Mn^{++} at a ratio of 2.11 leads to the initial formation of a large percentage of the trivalent Mn^{+++}, which having been formed dissociates but slowly into Mn^{++++}. This slow dissociation is probably due at least partly to the reversing action of the Mn^{++++} present.

The Oxidation Properties of Mn^{+++} and Mn^{++++}.—To determine which of these ions oxidizes Cr^{+++} more rapidly, it is necessary to measure the initial rate after a known change in the proportion of the Mn^{+++} to Mn^{++++}. Now decreasing the acidity causes a shift to the formation of Mn^{++++}, manganese dioxide eventually being precipitated during the course of the oxidation if the acidity has been sufficiently decreased, say from 2.92 M sulfuric acid to 1.46 M sulfuric acid.

Under conditions corresponding to the results expressed in Table V and Curve B, Fig. 2, but with the acidity decreased by a fraction, the initial linear rate of oxidation was measured. The results are shown in Table VII, where the usual sulfuric acid concentration, 2.92 M, is expressed as unity.

TABLE VII

EFFECT OF CHANGING THE SULFURIC ACID CONCENTRATION ON THE OXIDATION BY MANGANESE DIOXIDE DISSOLVED IN SULFURIC ACID

Relative sulfuric acid concentration	1	0.8	0.65	0.5
Linear rate of oxidation, cc. of $Cr_2O_7^{--}$/min.	0.238	0.332	0.348	0.396

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[9] Grube and Huberich, *Z. Elektrochem.*, **29**, 8 (1923).

That the tetravalent Mn^{++++} oxidizes the Cr^{+++} more rapidly is seen from the fact that decreasing the sulfuric acid concentration results in an increase in the rate of oxidation.

The slow but continuous dissociation of Mn^{+++} into Mn^{++++} in its approach to the equilibrium concentration is demonstrated by increasing the period of incubation between the MnO_4^- and Mn^{++} previous to adding the Cr^{+++}. The results are shown in Table VIII, where it is seen that increasing the incubation period results in an increase in the rate of oxidation.

TABLE VIII

EFFECT OF CHANGING THE MnO_4^-–Mn^{++} INCUBATION PERIOD

Incubation period, minutes	4	16	24	32
Linear rate of oxidation, cc. of $Cr_2O_7^{--}$/min.	0.228	0.238	0.250	0.268

The tendency of Mn^{+++} to enter into complex ion formation with anions is well known. If it exists in complex formation with sulfuric acid, so that the dissociation of the Mn^{+++} into Mn^{++++} and Mn^{++} is preceded by its liberation from the complex, this should be reflected in a greater increase in the initial rate for a given increase in the incubation period when the sulfuric acid concentration is diminished.

TABLE IX

EFFECT OF CHANGING THE MnO_4^-–Mn^{++} INCUBATION PERIOD—SULFURIC ACID CONCENTRATION REDUCED BY ONE-HALF TO 1.46 *M*

Incubation period, minutes	8	18
Linear rate of oxidation, cc. of $Cr_2O_7^{--}$/min.	0.294	0.396

Comparing the results of Table IX with those of Table VIII, it is seen that at the lower acidity the effect of changing the incubation period is considerably more marked.

Müller and Koppe[10] and Holluta and Obrist[11] have shown that in the presence of fluoride ion the reaction between MnO_4^- and Mn^{++} goes completely to the formation of a trivalent manganic fluoride complex. In Table X are given the results obtained in the oxidation of Cr^{+++} by this complex formed by adding NaF to the MnO_4^- before the addition of excess Mn^{++}.

TABLE X

EFFECT OF FLUORIDE ION ON THE OXIDATION OF Cr^{+++} ION BY MANGANESE DIOXIDE DISSOLVED IN SULFURIC ACID

$Mn^{++}/MnO_4^- = 4.22$. $F^-/Mn^{+++} = 4.04$

Minutes	10.62	20.62	40.73
$Cr_2O_7^{--}$ cc.	2.19	3.56	5.48

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[10] Müller and Koppe, *Z. anorg. Chem.*, **68**, 160 (1910).

[11] Holluta and Obrist, *Monatsh.*, **41**, 555 (1920).

Comparing the results of this table with those of Table VI, where the Mn^{++}/MnO_4^- ratio is also 4.22, it is seen that the rate of oxidation due to the fluoride ion complex is two-thirds that in the absence of fluoride ion. Such a small diminution in the rate leads again to the conclusion that in a 2.92 *M* sulfuric acid solution we have present primarily the $Mn^{+++} \cdot H_2SO_4$ complex rather than the free Mn^{+++}.

The Relative Proportion of Mn^{+++} and Mn^{++++} in Manganese Dioxide Dissolved in Sulfuric Acid.—In 2.92 *M* sulfuric acid, the addition of 2.11 moles of Mn^{++} per mole of MnO_4^- at 0.00144 *M* concentration leads as we have seen to the formation of 79% Mn^{+++} and 21% Mn^{++++}. How this proportion is affected by a change in the ratio can be determined by reference to Curve C, Fig. 2, where the ratio is only 0.42.

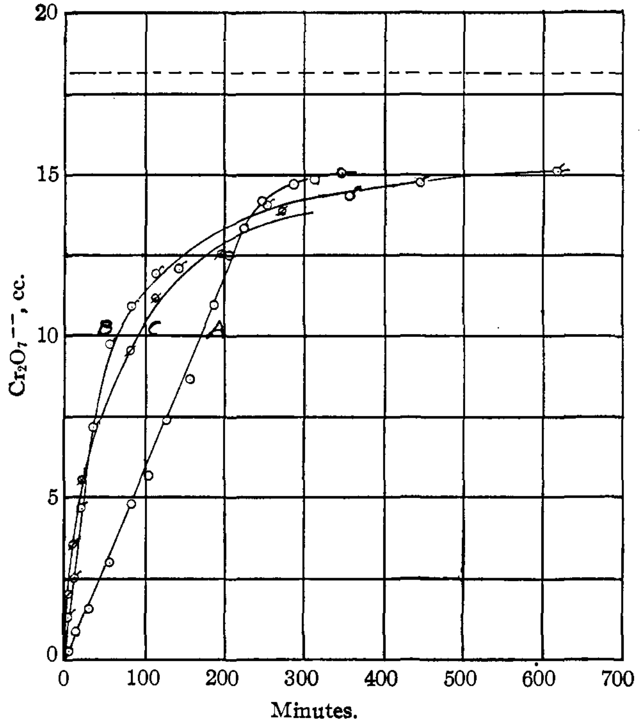

Fig. 2.—Oxidation of Cr^{+++} by manganese dioxide dissolved in sulfuric acid at 25.1°. Curve A, Mn^{++}/MnO_4^- = 0.42; Curve B, Mn^{++}/MnO_4^- = 2.11; Curve C, Mn^{++}/MnO_4^- = 4.22.

Here the curve is linear up to 14 cc. of $Cr_2O_7^{--}$. By the same method of calculation previously employed, it is found that the percentages are here, 22% Mn^{+++}, 78% Mn^{++++}. Thus it is seen that with a decrease in the ratio of Mn^{++} to MnO_4^- there is a large increase in the proportion of Mn^{++++} to Mn^{+++}.

The Interaction between Mn^{++} and Mn^{++++}, and the Mechanism of the Oxidation by Mn^{+++}.—The magnitude of the interaction between Mn^{++} and Mn^{++++} to give Mn^{+++} may be inquired into by determining the effect of excess Mn^{++} on the rate of oxidation of Cr^{+++} by MnO_2 in sulfuric acid. For if Mn^{++} reduces the Mn^{++++} to the less reactive Mn^{+++} ion, its effect in excess would be to diminish the rate of oxidation of the Cr^{+++} to $Cr_2O_7^{--}$.

We will first set down the results obtained on the addition of Zn^{++} and Fe^{+++} ions. Zinc sulfate and ferric sulfate were added to the MnO_4^- in sulfuric acid previous to the addition of the Mn^{++}, the Cr^{+++} then being added in the usual way.

Table XI*a*

Effect of Zn^{++} on the Oxidation of Cr^{+++} Ion by Manganese Dioxide Dissolved in Sulfuric Acid

$Mn^{++}/MnO_4^- = 2.11$

Ratio of Zn^{++}/Mn^{++++}	0.0	0.063	0.31	0.92
Linear rate of oxidation, cc. of $Cr_2O_7^{--}$/min.	0.238	0.315	0.285	0.290

Table XI*b*

Effect of Fe^{+++} on the Oxidation of Cr^{+++} Ion by Manganese Dioxide Dissolved in Sulfuric Acid

$Mn^{++}/MnO_4^- = 2.11$

Ratio of Fe^{+++}/Mn^{++++}	0.0	0.023	0.24
Linear rate of oxidation, cc. of $Cr_2O_7^{--}$/min.	0.238	0.280	0.300

In Tables XI*a* and XI*b* the concentrations of the Zn^{++} and Fe^{+++} are expressed as their ratio in moles to the Mn^{++++} that would be present if the latter alone were formed by interaction between MnO_4^- and Mn^{++}. It is seen that a slight addition of Zn^{++} or Fe^{+++} cation produces an increase in the linear rate of oxidation. Further addition of these cations produces but little increase in the rate.

Having thus determined what the effect of Mn^{++} should be in its capacity as a cation, we set down in Tables XII*a* and XII*b* the results which

Table XII*a*

Effect of Excess Mn^{++} on the Oxidation of Cr^{+++} Ion by Manganese Dioxide Dissolved in Sulfuric Acid

MnO_4^- concentration, 0.000576 *M*

Ratio of Mn^{++}/MnO_4^-	2.11/1	7.38/1	15.8/1
Cc. of $Cr_2O_7^{--}$ after ten minutes	0.626	0.473	0.306

Table XII*b*

Effect of Excess Mn^{++} on the Oxidation of Cr^{+++} Ion by Manganese Dioxide Dissolved in Sulfuric Acid

MnO_4^- concentration, 0.000288 *M*

Ratio of Mn^{++}/MnO_4^-	2.11/1	10.5/1
Cc. of $Cr_2O_7^{--}$ after ten minutes	0.225	0.108

were obtained with Mn^{++} in excess. The degree of oxidation after ten minutes is recorded against the ratio of Mn^{++} to MnO_4^-.

The effect of Mn^{++} in ratio greater than 4, contrary to the effect of the Zn^{++} and Fe^{+++} cations, is a progressive decrease in the oxidation rate as the ratio is increased.

We have already seen that the apparent oxidation rate of Mn^{++++} is greater than that of Mn^{+++}. The above results with Mn^{++} ion in excess can be explained then on the basis of a greater interaction between Mn^{++++} and the excess Mn^{++} to give the Mn^{+++} ion, as expressed in Equation 3.

Whence does the Mn^{++++} ion arise? This question is pertinent since we have seen that the greater the initial ratio of Mn^{++} to MnO_4^- the greater the proportion of Mn^{+++} which is formed. At a ratio exceeding 4, we should expect the formation solely of Mn^{+++}.

On this basis, the Mn^{++++} which interacts with the excess Mn^{++} comes from the subsequent dissociation of the Mn^{+++} initially formed. It thus appears that the oxidation of Cr^{+++} by Mn^{+++} is at least in part indirect, taking place in virtue of its dissociation into the reactive Mn^{++++}. The apparent oxidation rate of the Mn^{+++} decreases in the presence of excess Mn^{++} due to the greater reversal of this dissociation.

The potential of Mn^{+++} against Mn^{++} in 4.55 *M* sulfuric acid, decreasing with the acidity, is given by Grube and Huberich[9] as 1.503 v. Landolt-Börnstein "Tabellen," **1923**, cite the normal electrode potential of $HCrO_4^-$ against Cr^{+++} as 1.3 v. The closeness of these values makes it appear likely that the oxidation of Cr^{+++} by Mn^{+++} is entirely indirect. Assuming this to be the case, the mechanism of the oxidation by the trivalent manganese is as follows.

I $Mn(HSO_4)_3$ [complex] $\rightleftarrows Mn^{+++} + 3HSO_4^-$
IIa $Mn^{+++} + Mn(HSO_4)_3 = Mn^{++++} + Mn^{++} + 3(HSO_4)^-$
IIb $2\,Mn^{+++} = Mn^{++++} + Mn^{++}$
III $Mn^{++++} + Mn^{+++} + Cr^{+++} + 4H_2O = CrO_4^{--} + 2Mn^{++} + 8H^+$

In Stage I we have the disengagement of the Mn^{+++} from its complex with the sulfuric acid. In Stages IIa and IIb the Mn^{+++} dissociates to form Mn^{++++}. In the third stage the Mn^{++++} oxidizes the Cr^{+++}, in conjunction with Mn^{+++}.

Skrabal[4] assumed that the rate of oxidation of oxalic acid in the presence of excess Mn^{++} was determined by the rate of dissociation of the Mn^{+++} ion from its oxalic acid complex. This rate of dissociation he found to be unimolecular. Dey and Dhar[6] found the oxidation of lactic and citric acids by the trivalent manganese also to be unimolecular.

If in accordance with these results we assume the rate of oxidation of Cr^{+++} in excess to be determined by the rate of the unimolecular disengagement of Mn^{+++} from its sulfuric acid complex we have

$$\frac{dx}{dt} = k_1\,(a - x) \tag{4}$$

x is here the equivalent concentration of $Cr_2O_7^{--}$, a is the initial equivalent (or molar) concentration of Mn^{+++}, while $(a - x)$ is the molar concentration of the trivalent manganese at any instant.

Now the above equation is strictly true only when the tetravalent manganese, whose concentration is negligible against the trivalent manganese, is used up solely in its reduction by the Cr^{+++}. However, a fraction of it is reduced to Mn^{+++} by the excess manganous ion according to (3) as we have shown.

Let b represent the initial molar excess of Mn^{++}, so that $b + x$ is the concentration of Mn^{++} at any instant.

The rate of reduction of Mn^{++++} by Mn^{++} is given by the equation

$$R_1 = k_3\,Mn^{++++}\,(b + x) \tag{5}$$

The rate of reduction of Mn^{++++} by the Cr^{+++} in excess is, according to Stage III above, given by

$$R_2 = k_2\,Mn^{++++}\,(a - x) \tag{6}$$

From (5) and (6) the fraction of the Mn^{++++}, formed by the dissociation of the Mn^{+++}, which is reduced by the Cr^{+++} as against reduction by the Mn^{++} is

$$F = \frac{k_2\,(a - x)}{(k_3 b + k_2 a) + (k_3 - k_2)x} \tag{7}$$

To take this reducing action of Mn^{++} into account a correction must be made to Equation 4 such that it is multiplied by the fraction F. We thus obtain finally for the rate of formation of $Cr_2O_7^{--}$

$$\frac{dx}{dt} = \frac{k_a\,(a - x)^2}{(k_b + x)} \tag{8}$$

where

$$k_a = \frac{k_1 k_2}{k_3 - k_2} \tag{9}$$

$$k_b = \frac{k_3 b + k_2 a}{k_3 - k_2} \tag{10}$$

This equation may be integrated and reduced to the form given by (11), where K_2 and K_1 represent a bi- and unimolecular velocity constant, respectively

$$(k_b + a)K_2 - K_1 = k_a \tag{11}$$

If we plot K_1 against K_2 we should by Equation 11 obtain a straight line whose slope is $(k_b + a)$ and whose intercept is k_a. From the smoothed data of Table VI, K_2 and K_1 were calculated and plotted against each other as shown in Fig. 3. A straight line is obtained with a slope of 23.0 and intercept -0.0088. With $a = 18.2$ cc., this gives $k_a = 0.0088$ and $k_b = 4.8$. Solving for k_3/k_2 and for k_1 by Equations 9 and 10, with $b = 0.73$, we obtain $k_3/k_2 = 5.61$ and $k_1 = 0.0406$. The specific rate of reduction of Mn^{++++} by Mn^{++} is thus 5.61 times as great as that by Cr^{+++} in excess, while the constant for the unimolecular decomposition at 25° of the complex, $Mn(HSO_4)_3$, is 0.0406.

At 35.0° the results obtained in the oxidation of Cr^{+++} by Mn^{+++} are shown in Table XIII.

TABLE XIII

OXIDATION OF Cr^{+++} BY MANGANESE DIOXIDE IN SULFURIC ACID AT 35.0°

Ratio of $Mn^{++}/MnO_4^- = 4.22$. $MnO_4^- = 0.001440$ *M*

Minutes	4.00	9.55	19.90	35.00	56.95	89.42	149.3
$Cr_2O_7^{--}$, cc.	4.90	7.62	10.11	12.11	13.69	14.78	15.70

Calculation from the straight line obtained in plotting K_1 against K_2 (Fig. 4) shows that at 35.0° $k_3/k_2 = 4.37$, $k_1 = 0.163$. The temperature coefficient of the unimolecular decomposition of the complex $Mn(HSO_4)_3$ is therefore 4.01.

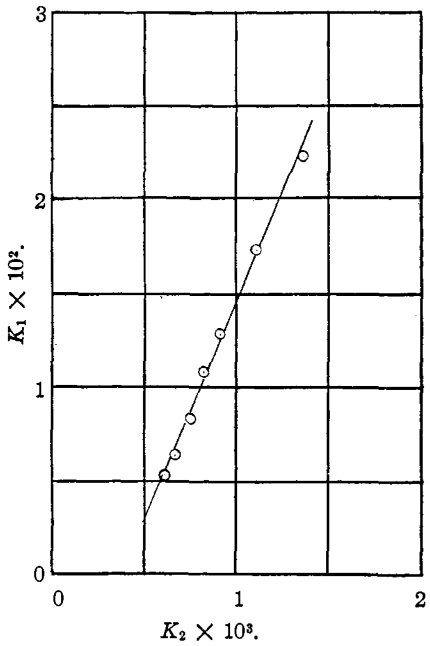

Fig. 3.—Oxidation of Cr^{+++} by manganese dioxide dissolved in sulfuric acid at 25.1°. $Mn^{++}/MnO_4^- = 4.22$.

Order of the Oxidation by Manganese Dioxide Dissolved in Sulfuric Acid.—In the oxidation by manganese dioxide in sulfuric acid solution the order of the reaction with respect to Cr^{+++} is unity as is seen from the data of Table XIV.

The initial linear rate of oxidation is here 0.011 cc./min. as against 0.024 cc./min. when the Cr^{+++} concentration is twice as great (Table V).

In the presence of a mixture of tri- and tetravalent manganese we should expect in accordance with Stage III of the above reaction a bimolecular oxidation of the Cr^{+++} (in excess). Keeping the ratio constant at 2.11, where, at $MnO_4^- = 0.00144$ *M*, we have 79% of Mn^{+++}, 21% of Mn^{++++}, the initial linear rate of oxidation was measured with varying MnO_4^- concentration. The results are shown in Table XV.

TABLE XIV

OXIDATION OF Cr^{+++} BY MANGANESE DIOXIDE IN SULFURIC ACID AT 25.1°

Cr^{+++} concentration reduced by $^1/_2$. Ratio of $Mn^{++}/MnO_4^- = 2.11$

Minutes	6.25	18.12	38.08	69.62	140.2	221.9	328.8	442.4
$Cr_2O_7^{--}$, cc.	0.60	1.84	4.74	7.94	10.48	11.97	13.10	13.80

TABLE XV

INITIAL LINEAR RATE OF OXIDATION WITH CHANGE IN THE MANGANESE DIOXIDE CONCENTRATION

Relative manganese dioxide concentration	2.0	1.0	0.4	0.2[a]
$Cr_2O_7^{--}$, cc./min.	0.665	0.238	0.060	0.021

[a] The Mn^{++} remained in contact with the MnO_4^- for forty-five instead of the usual sixteen minutes.

If we plot the log of the rate of oxidation against the relative concentration, we obtain very closely a straight line whose slope is 1.5. This is therefore the apparent order of the oxidation of Cr^{+++} in excess by a mixture of the tri- and tetravalent manganese.

Now we have already observed that decreasing the concentration of Mn^{++} relative to MnO_4^- results in a shift in the proportion of Mn^{++++} to Mn^{+++} in favor of the tetravalent ion. The apparent fractional order of reaction found above can be explained on the basis of a similar shift with a decrease in the initial Mn^{++} concentration, though here the MnO_4^- concentration also changes.

Properties of the Reduction of MnO_4^- in Acid Solution.—We have shown that the oxidation by MnO_4^- in acid solution is accompanied by the oxidation due to the direct action of the tetravalent and the indirect action of the trivalent manganese. MnO_4^- itself oxidizes Cr^{+++} very slowly at 25°; Mn^{++++} oxidizes it rapidly. The action of Mn^{+++} takes place in virtue of its unimolecular disengagement from a complex compound with sulfuric acid with subsequent dissociation into Mn^{++++}. The latter is responsible for the oxidation of the Cr^{+++}.

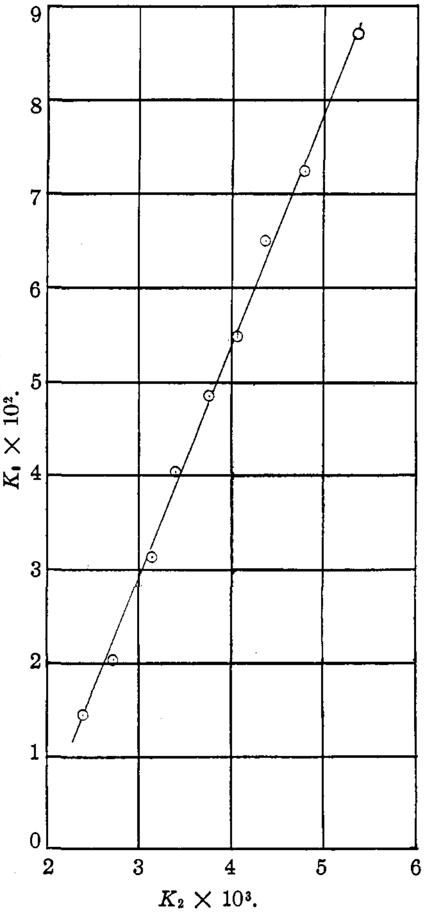

Fig. 4.—Oxidation of Cr^{+++} by manganese dioxide dissolved in sulfuric acid at 35.0°. $Mn^{++}/MnO_4^- = 4.22$.

Mn^{++} reduces Mn^{++++} to the trivalent state. Thus the oxidation of Cr^{+++} by Mn^{+++} is retarded in proportion to the excess Mn^{++} present.

Since, ultimately, only Mn^{+++} in its usual complex form and an increasing excess of Mn^{++} are present, the marked end retardation observed in the oxidation of Cr^{+++} by MnO_4^- is explained.

We have shown that the interaction between Mn^{++} and MnO_4^- in 2.92 *M* sulfuric acid leads initially to the formation of Mn^{+++} and Mn^{++++}. The proportion of the latter is increased at a fixed MnO_4^- concentration by decreasing the Mn^{++} concentration.

On this basis, in the course of the oxidation of Cr^{+++} by MnO_4^-, the Mn^{++} which is first liberated forms the reactive Mn^{++++}. As the concentration of Mn^{++} tends to build up relative to the MnO_4^-, more and more of the trivalent manganese is formed, thus slowing up the autocatalysis until finally, since it alone is present, its own slow oxidation rate is measured.

The results obtained here in the reduction of MnO_4^- by Cr^{+++} show in several respects a striking similarity to the reduction by oxalic, tartaric and citric acids, etc. The chief difference lies in the fact that here the Mn^{+++} forms a complex with sulfuric acid, while there it forms a complex which is probably more stable with the reducing agent itself. By assuming as above an indirect oxidation by the Mn^{+++} complex and a very rapid oxidation by the Mn^{++++}, the properties of the permanganate reduction by these organic acids may be readily explained. In particular the so-called induction observed by Skrabal[4] in the oxidation of oxalic acid can be accounted for by the formation in the presence of slight amounts of Mn^{++} of the highly reactive Mn^{++++} by interaction between MnO_4^- and Mn^{++}.

Summary

The reduction of MnO_4^- by Cr^{+++} at 25.1° in sulfuric acid solution is autocatalytic and resembles closely the reduction by numerous organic acids, such as oxalic acid.

A study of the mechanism of the reaction reveals the presence of Mn^{++++} and of Mn^{+++} which is contained in a sulfuric acid complex. Oxidation by the latter is indirect in virtue of its unimolecular disengagement from the complex and its subsequent decomposition into Mn^{++++}, which oxidizes Cr^{+++} rapidly. The temperature coefficient between 25 and 35° of the unimolecular reaction is 4.01. Mn^{++++} also reacts with Mn^{++}, thus reverting to the non-reactive Mn^{+++}.

In the interaction between Mn^{++} and MnO_4^- in acid solution, the relative proportion of Mn^{++++} to Mn^{+++} increases with decrease in the ratio of Mn^{++} to MnO_4^-.

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