Some isotopic exchange reactions of manganese

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Some isotopic exchange reactions of manganese

Abstract
Isotopic exchange experiments with Mn-54 have been conducted with various chemical forms of manganese in existence during the reaction between Mn++ and MnO-4 in acid solutions to produce a hydrous oxide containing manganese (IV).

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SOME ISOTOPIC EXCHANGE REACTIONS OF MANGANESE

By
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January 27, 1955

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Ames, Iowa
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>INTRODUCTION.</strong></td>
<td>1</td>
</tr>
<tr>
<td><strong>EXPERIMENTAL.</strong></td>
<td>6</td>
</tr>
<tr>
<td>Materials</td>
<td>6</td>
</tr>
<tr>
<td>Preparation of Solutions</td>
<td>7</td>
</tr>
<tr>
<td>Active manganese (II) perchlorate</td>
<td>7</td>
</tr>
<tr>
<td>Potassium permanganate.</td>
<td>8</td>
</tr>
<tr>
<td>Manganese (II) perchlorate.</td>
<td>8</td>
</tr>
<tr>
<td>Tetraphenylarsenium nitrate</td>
<td>8</td>
</tr>
<tr>
<td>Counting Method.</td>
<td>8</td>
</tr>
<tr>
<td>Preparation of samples for counting</td>
<td>8</td>
</tr>
<tr>
<td>Counting of samples</td>
<td>9</td>
</tr>
<tr>
<td>Correction of counting data</td>
<td>9</td>
</tr>
<tr>
<td>Analyses</td>
<td>10</td>
</tr>
<tr>
<td>Colorimetric analysis</td>
<td>10</td>
</tr>
<tr>
<td>Analysis of tetraphenylarsenium precipitates</td>
<td>10</td>
</tr>
<tr>
<td><strong>PROCEDURE AND RESULTS</strong></td>
<td>12</td>
</tr>
<tr>
<td>Manganese (II) -- Manganese Dioxide Exchange</td>
<td>12</td>
</tr>
<tr>
<td>Exchange in the Guyard Reaction.</td>
<td>13</td>
</tr>
<tr>
<td>Manganese (II) -- Permanganate Exchange</td>
<td>15</td>
</tr>
<tr>
<td>Spectrophotometric Examination of Guyard Mixtures</td>
<td>17</td>
</tr>
<tr>
<td>Rate of Manganese (II) -- Permanganate Exchange</td>
<td>19</td>
</tr>
<tr>
<td><strong>DISCUSSION.</strong></td>
<td>25</td>
</tr>
<tr>
<td>Manganese (II) -- Manganese Dioxide Exchange</td>
<td>25</td>
</tr>
<tr>
<td>Exchange in the Guyard Reaction.</td>
<td>30</td>
</tr>
<tr>
<td>Manganese (II) -- Permanganate Exchange</td>
<td>31</td>
</tr>
<tr>
<td>Spectrophotometric Investigation</td>
<td>32</td>
</tr>
<tr>
<td><strong>SUMMARY</strong></td>
<td>35</td>
</tr>
<tr>
<td><strong>LITERATURE CITED.</strong></td>
<td>35</td>
</tr>
</tbody>
</table>
SOME ISOTOPIC EXCHANGE REACTIONS
OF MANGANESE*

by

James A. Happe and Don S. Martin, Jr.

ABSTRACT

Isotopic exchange experiments with Mn$^{54}$ have been conducted with various chemical forms of manganese in existence during the reaction between Mn$^{++}$ and MnO$_4^-$ in acid solutions to produce a hydrous oxide containing manganese(IV). It was found that 30 to 40 per cent exchange between the freshly formed precipitates and Mn$^{++}$ occurred within 1 to 2 minutes but that additional exchange was negligible over 20 to 30 minutes. Although a fraction of the MnIV of the precipitates exchanged with Mn$^{++}$, a portion of it was very quickly excluded from rapid exchange. However, a complete isotopic equilibrium during the overall reaction between Mn$^{++}$ and MnO$_4^-$ required that MnO$_4^-$ was completely reduced to MnIV before the growth of precipitate grams. Tetraphenylarsonium permanganate was precipitated from solutions of MnO$_4^-$ and Mn$^{**}$++ in 1-2 molar HNO$_3$ before the onset of the precipitation of MnO$_2$ which occurred at ca. 10 hours. The permanganate fraction had gained enough activity to correspond to an exchange half-time of 12 hours. Spectrophotometric studies showed that before a precipitate appeared at least 40 per cent of the MnO$_4^-$ was reduced by a reaction approximately first order in MnO$_4^-$ and without an induction period. In the presence of such large amounts of intermediate species, the exchange between MnO$_4^-$ and Mn$^{++}$ or MnIV may not be real.

*This report is based on a Master's thesis by James A. Happe submitted January, 1955 to Iowa State College, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.
INTRODUCTION

In recent years the preparation of suitable radioactive isotopes of nearly all of the elements has placed in the hands of the chemist a powerful new tool. One of the most interesting applications of these so called "tagged atoms" in the field of chemistry has been the study of exchange reactions. Frequently, a knowledge of such phenomena has proved to be of great value in the description of reaction mechanisms. The mechanism involved in the reaction\(^1\) between manganese (II) ions and permanganate to form manganese dioxide, as represented by

\[
3 \text{Mn}^{++} + 2 \text{Mn}O_4^- + 2 \text{H}_2\text{O} \rightarrow 5 \text{MnO}_2 + 4\text{H}^+,
\]

has been the subject of much speculation. A study of the exchange taking place in the course of this reaction is the subject of this work. Three exchange systems have been investigated in this study: the manganese (II) -- manganese dioxide system, the manganese (II) -- permanganate system before precipitation occurs, and the overall manganese (II) -- permanganate system forming manganese dioxide.

The work of Gorgcau, Guyard, and Harcourt and Esson (1, 2, 3) gave an early indication of the actual reaction taking place when permanganate and manganese (II) are mixed. If one investigates the volume of work presented on this reaction in the literature of the past eighty years, he is at once impressed with the variety of experimental evidence reported. Proposed mechanisms are frequently contradictory. Although recent investigation of exchange reactions has clarified several controversial points, it is felt that a historical résumé of the work done on the reaction may be of value.

In their investigation of the reaction between permanganate and oxalic acid in the presence of manganese (II), Harcourt and Esson (3) observed

\[^1\]This reaction has become known as the Gorgcau reaction after one of its early investigators. It will frequently be convenient to refer to it as such in this paper.

\[^2\]The term manganese dioxide will be used to refer to the precipitate obtained from the reaction between manganese (II) and permanganate. It is recognized that the precipitates may have a variable degree of hydration and also, from the observed stoichiometry, it was noted that the precipitates must contain some manganese in oxidation states lower than four.
that the rate of the reaction is markedly increased by an increase in the concentration of manganese (II) or hydrogen ion. On the other hand, addition of oxalate ion had a complex effect, first increasing the rate and then decreasing it as the concentration of oxalate became large. They concluded that the reaction proceeded in two stages. The first, being the faster, consisted of the reduction of permanganate by manganese (II) yielding manganese dioxide. The second consisted of the reduction of the dioxide to manganese (II). In order to explain their results, they proposed that after its formation, the manganese dioxide was attacked by both oxalic acid and manganese (II). The latter reaction formed manganese (III) which in turn was reduced by oxalate ion. The mechanism they proposed was the following:

\( (2) \quad 2 \text{Mn(OH)}_7 + 5 \text{H}_2\text{C}_2\text{O}_4 \rightarrow 2 \text{Mn(OH)}_2 + 10 \text{CO}_2 + 10 \text{H}_2\text{O} \) (very slow)

\( (3) \quad 3 \text{Mn(OH)}_2 + 2 \text{Mn(OH)}_7 \rightarrow 5 \text{Mn(OH)}_4 \) (very fast)

\( (4) \quad \text{Mn(OH)}_4 + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{Mn(OH)}_2 + 2 \text{CO}_2 + 2 \text{H}_2\text{O} \) (fast).

Scrabal \((4)\), as a result of his studies on the oxalate reduction of permanganate in the presence of manganese (II), included in his mechanism a measurably fast reaction between permanganate and oxalate to form manganese (II). This was followed by a rapid reaction between permanganate and manganese (II) to produce manganese (III). He concluded that the manganese (III) was then converted into an oxalate complex which dissociated at a measurable rate.

Evidence presented by Launer \((5)\) and Launer and Yost \((6)\) in a series of two articles showed that the measurable step in the oxalate--permanganate--manganese (II) reaction was the reduction of manganese (III) by oxalate ion rather than the dissociation of the oxalate complex. In addition to proposing the existence of the \(\text{CO}_2^2\) ion, he also forwarded the concept of a rapid initial equilibrium between permanganate, manganese (II) and manganese (IV). The accelerating effect of oxalate ion on the manganese (II)--permanganate reaction was attributed to a shift in equilibriums \((5)\) and \((6)\) as a result of the removal of manganese (III) by complex formation. The mechanism proposed was the following:

\( (5) \quad \text{MnO}_4^- + \text{Mn}^{++} \leftrightarrow \text{Mn}^{+++} \) (rapid, reversible)

\( (6) \quad \text{Mn}^{+++} + \text{Mn}^{++} \leftrightarrow 2 \text{Mn}^{+++} \) (rapid, reversible)

\( (7) \quad \text{Mn}^{+++} + \text{C}_2\text{O}_4^- \rightarrow \text{Mn}^{+++} + \text{CO}_2 + \text{CO}_2^- \) (measurable)

\( (8) \quad \text{Mn}^{+++} + \text{CO}_2^- \rightarrow \text{CO}_2 + \text{Mn}^{+++} \) (rapid)

\( (9) \quad \text{Mn}^{+++} + \text{C}_2\text{O}_4^- \leftrightarrow \text{Mn(C}_2\text{O}_4)^+ \) (rapid, reversible)
The work of Cartledge and Bricks (7), Taube (8) and others (5, 9, 10, 11, 12, 13) has since afforded us a highly acceptable explanation for the slow second stage of the oxalate--permanganate reaction. For an excellent survey of this point, the reader is referred to a recent article by R. N. Woes (14). Several other investigators have published works on the oxalate reduction of permanganate and these may be found under references (15, 16, 17, 18, 19, 20, 21). They are of interest here as a result of their very direct connection to the manganese (II)--permanganate reaction.

The first application of radioactive manganese to the Guyard reaction was that of Polissar (22) in his investigation of the exchange occurring between various oxidation states of manganese. His objective lay mainly in the discovery of any rapid exchange taking place. Prompted by the repeated proposals of a rapid equilibrium of the type,

\[ \text{Mn}^{\text{II}} + \text{MnO}_4^- \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} \text{Mn}^{\text{IV}} \text{ or MnIII}, \]

he carried out the following experiment. A relatively small amount of tagged manganese (II) was added to a large excess of permanganate in a perchloric acid solution. The exchange reaction was terminated when desired by the rapid addition of sodium hydroxide. This brought about the precipitation of the manganese (II) as manganese dioxide.

If a rapid equilibrium such as reaction (12) existed, essentially all of the activity added would be found in the permanganate filtrate. If, on the other hand, the activity was found in the manganese dioxide precipitate, the existence of this type of rapid equilibrium could be ruled out. Times up to fifteen minutes were employed and the results indicated that no exchange had occurred. As pointed out by Polissar (22), the existence of a rapid equilibrium such as

\[ 3 \text{Mn}^{\text{II}} + \text{MnO}_4^- \rightleftharpoons 3 \text{Mn}^{\text{III}} + \text{Mn}^{\text{IV}} \]

or

\[ \text{Mn}^{\text{II}} + 2 \text{MnO}_4^- \rightleftharpoons \text{Mn}^{\text{IV}} + 2 \text{Mn}^{\text{VI}} \]

would not be contradictory to his results provided the products did not undergo a rapid exchange.

Other systems investigated for exchange by Polissar (22) were manganese dioxide--permanganate, manganese dioxide--manganese (II), manganese (III)
oxalate complex--manganese (II), and manganese (III) oxalate complex--permanganate. In systems one, two, and four the maximum exchange times employed were, respectively, two minutes, two minutes, and thirty seconds. No exchange was observed. In system number three, however, complete exchange was found in five seconds. The simplest interpretation of this rapid exchange would be, according to Polissar (22), the well known equilibrium,

\[(15) \text{Mn}^{IV} + \text{Mn}^{III} \rightleftharpoons 2 \text{Mn}^{III} \text{ (rapid, reversible).}\]

Waterbury and Martin (23) have recently added support to this interpretation by carrying out a kinetic study of the manganese (II), -(III), -(IV) equilibrium in iodic acid solution. By using a colorimetric method, they have found the equilibrium to be established in less than ten seconds at room temperature. A value of \(2.5 \times 10^{12}\) was given for the equilibrium constant at \(0^\circ\text{C}\), the proposed reaction being:

\[(16) \text{Mn}^{IV} \text{O(OH)}(\text{IO}_3)_4^{3-} + 3 \text{H}^+ + 4 \text{IO}_3^- + \text{Mn}^{++} \rightleftharpoons 2 \text{Mn} \text{(IO}_3\text{)}_4^{-} + 2 \text{H}_2\text{O}.\]

Adamson (24), on the other hand, as a result of his exchange studies on the manganese (II)--permanganate system, has expressed the opinion that the rapid exchange observed by Polissar (22) is due to species partially combined in a complex, for example:

\[(17) \text{Mn(C}_2\text{O}_4\text{)}_2 + \text{Mn}^{++} \rightleftharpoons 2 \text{Mn(C}_2\text{O}_4\text{)}^+.\]

The manganese (II), -(III), -(IV) equilibrium was thus assumed to be relatively unimportant in the absence of complex forming agents. In an attempt to verify this assumption, Adamson (24) has investigated the manganese (II)--manganese (III) exchange in perchloric acid solution. Exchange times of the order of ten to twenty seconds were obtainable and extensive exchange was observed. The results, however, would appear to be rather inconclusive.

In investigating the exchange between manganese (II) and permanganate, Adamson (24) has used a method similar to that adopted by Polissar (22). The reaction was carried out in the presence of excess permanganate and was terminated when desired by causing the precipitation of the active manganese (II) as manganese dioxide. By working in solutions approximately three molar in perchloric acid, the appearance of manganese dioxide could be delayed for periods up to about four hours. Thus exchange times far in excess of those employed by Polissar (22) were available. Under these conditions a slow exchange of approximately three and one half hours half-time was indicated. Substitution of sulfuric acid for perchloric acid had no marked effect on the exchange. The presence of fluoride ion essentially prevented any exchange. An attempt was made to determine the dependence of the exchange rate on the concentrations of manganese (II), permanganate and hydrogen ions. In order to explain the observed slow exchange, the following mechanism was proposed:
(18) \[ 6 \text{H}^+ + \text{MnO}_4^- + 3 \text{Mn}^{2+} \rightleftharpoons 3 \text{Mn}^{3+} + \text{MnO}^{2+} + 3 \text{H}_2\text{O} \] (rapid, reversible)

(19) \[ \text{Mn}^{\text{III}} + \text{Mn}^{\text{IV}} \rightarrow \text{Slow electron exchange.} \]

It might be pointed out here that Adamson (24) has assumed that no appreciable chemical reaction occurs in the permanganate-manganese (II) mixture until the appearance of manganese dioxide.

Tomkins (25) has employed a type of turbidimeter to make a kinetic study of the manganese (II)-permanganate reaction. He has shown that the autocatalysis observed in the Guyard reaction is due to manganese dioxide and is probably a surface reaction. In order to satisfy his kinetic data, he proposed a mechanism which included a rapid initial equilibrium between manganese (II), permanganate, manganese (III) and manganese (VI), equation (20). This was followed by a rapid manganese (II), -(III), -(IV) equilibrium, equation (15), and a slow hydrolysis of manganese (IV) to the dioxide.

(20) \[ \text{Mn}^{\text{II}} + \text{MnO}_4^- \rightleftharpoons \text{Mn}^{\text{III}} + \text{Mn}^{\text{VI}}. \]

As pointed out by Hayes (26), however, the mechanism is unsatisfactory since it requires that 40% of the manganese dioxide precipitate be formed from the reaction between manganese (VI) and manganese (II), although this reaction is stated to be slow and of only secondary importance.

Manganese (III) and manganese (VI) have also been proposed by Waterbury, Hayes and Martin (27) as the initial products in the manganese (II)-permanganate reaction. This conclusion together with the rapid manganese (II), -(III), -(IV) equilibrium form the basis of a mechanism offered for the periodic oxidation of manganese (II) to permanganate. A colorimetric method was employed in a kinetic study of the latter reaction.

Although several authors (22, 28, 29, 30) have reported on the exchange between manganese (II) and manganese dioxide, the results obtained would appear rather inconsistent. Reported exchanges have ranged from zero to one hundred per cent. Probably the most complete work yet presented has been that of Jordan (30). His paper describes studies on the exchange occurring between manganese (II) and a variety of oxides of manganese. As a result of his experiments with an oxide containing only manganese (II), it was concluded that such an oxide was susceptible to complete exchange with a manganese (II) salt in solution. The exchange, however, amounted to only about twenty per cent at room temperature due presumably to structural hindrances by the crystals. Oxides containing only manganese (IV), on the other hand, were found to be incapable of any significant exchange. In view of these results, an explanation was offered for the complex exchange observed with oxides containing both manganese (II) and manganese (IV). The very rapid exchange taking place initially with these oxides was
attributed to a rapid exchange between manganese (II) in the solution and manganese (II) contained in the oxide. The slow exchange which followed was hence attributed to a manganese (II)--manganese (IV) exchange through the operation of reaction (15).

Pullman and Haissinsky (29) have also reported that a rapid initial exchange of approximately forty per cent takes place between manganese (II) and manganese dioxide within the first fifteen minutes of contact. Further exchange was found to be very slow.

EXPERIMENTAL

Materials

Potassium permanganate, KMnO₄: Baker and Adamson reagent grade.
Manganese sulfate, MnSO₄: Baker and Adamson reagent grade.
Sodium bromate, NaBrO₃: Baker's analyzed chemical reagent.
Potassium periodate, KIO₄: Baker's analyzed chemical reagent.
Sodium oxalate, Na₂C₂O₄: Baker's analyzed chemical reagent.
Nitric acid, HNO₃: Baker and Adamson reagent grade. Sp. Gr. 1.42; 70% HNO₃.
Sulfuric acid, H₂SO₄: Dupont reagent grade. Sp. Gr. 1.84; 95-98% H₂SO₄.
Perchloric acid, HClO₄: Baker and Adamson reagent grade. 70-72% HClO₄.
Hydrogen peroxide, H₂O₂: Baker and Adamson reagent grade. 30% H₂O₂.

These chemicals as well as all others used were of a quality to meet A.C.S. standards.

The water used in the preparation of solutions and in the exchange experiments was obtained by redistillation of laboratory distilled water from alkaline permanganate solution.

Active Manganese: The manganese activity used in these exchange studies was provided by Dr. A. L. Thompson of the McGill University Radiation Laboratory, Montreal, Quebec. The active isotope, manganese 54, was produced by irradiation of manganese metal with approximately 80 mev. deuterons from the laboratory cyclotron, the reaction being: Mn⁵⁵ (d,p2n) Mn⁵⁴. This isotope decays by electron capture and is characterized by a K X-ray in coincidence with a 0.8m ev. gamma ray. The half-life is conveniently long, being 310 days.
Preparation of Solutions

Active manganese (II) perchlorate

Since it was desired to carry out exchange reactions in solutions which contained perchlorate as the only anion, the active manganese metal was converted to a solution of manganese (II) perchlorate. Perchlorate solutions were used so that complex formation phenomena would be minimized. Since long-lived activities in addition to manganese 54 were undoubtedly produced in the manganese metal during its irradiation, a preparative procedure was necessary which would result in a radiochemically pure solution of manganese (II) perchlorate. The presence of such foreign activities might interfere by their adsorption on precipitates. As a result, the following method was adopted, making use of the high adsorptive properties of iron (III) hydroxide.

Approximately two hundred milligrams of active manganese were dissolved in nitric acid and a small amount of iron (III) nitrate was added as a carrier for impurities. A basic acetate separation of the iron from manganese was then carried out as described by Scott (31). The manganese remaining in the filtrate was then oxidized to manganese dioxide by means of sodium bromate and, after filtration, was dissolved in hydrogen peroxide slightly acidified with sulfuric acid. Iron (III) was again added as a carrier and the basic acetate separation of iron from manganese repeated.

After oxidation of the manganese to the dioxide and its subsequent solution in hydrogen peroxide, the following hold back carriers were added to the solution: chromium as chromium (III) sulfate, calcium as calcium (II) nitrate, iron as iron (III) nitrate, yttrium as the nitrate, titanium as titanium sulfate, and vanadium as ammonium metavanadate. The manganese in the solution was then oxidized to manganese dioxide. After filtering off the solid and redissolving it in hydrogen peroxide, the above hold back carriers were again added and the oxidation to manganese dioxide repeated. In order to insure removal of remaining traces of carriers carried down with the manganese precipitates, two further bromate oxidations to the dioxide were carried out followed by a basic acetate separation and a third oxidation to manganese dioxide. The final sample of manganese dioxide was dissolved in a minimum amount of hydrogen peroxide acidified with perchloric acid and after the removal of excess peroxide by continued boiling with a small amount of platinum black, the solution was filtered and diluted to a volume of one hundred milliliters. The pH of the solution was found to be 1.5 and colorimetric analysis showed it to be 0.3370 molar in manganese (II) perchlorate.

An indication as to the effectiveness of the purification may be obtained from Table 1 in which the amounts of activity found in the three iron (III) hydroxide precipitates and the two samples of hold back carriers are given.
Table 1

Indication as to the effectiveness of purification of the active manganese (II).

<table>
<thead>
<tr>
<th>Sample counted</th>
<th>Counts/min.</th>
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<tr>
<td>Fe (OH)₃ #1</td>
<td>5290</td>
</tr>
<tr>
<td>Fe (OH)₃ #2</td>
<td>79</td>
</tr>
<tr>
<td>Fe (OH)₃ #3</td>
<td>8</td>
</tr>
<tr>
<td>Carriers #1</td>
<td>33</td>
</tr>
<tr>
<td>Carriers #2</td>
<td>39</td>
</tr>
</tbody>
</table>

Potassium permanganate

Permanganate solutions were prepared by dissolving reagent grade potassium permanganate in redistilled water and heating this solution at a temperature slightly below the boiling point for approximately one hour. After allowing the solution to stand over night, it was filtered and diluted to the desired volume. Permanganate solutions were standardized against sodium oxalate according to the method of Fowler and Bright (32).

Manganese (II) perchlorate

These solutions were prepared from reagent grade manganese (II) sulfate by dissolving this reagent in water and oxidizing the manganese to manganese dioxide. The solution was filtered and the solid dissolved in hydrogen peroxide slightly acidified with perchloric acid. After removal of the excess peroxide, the manganese content of the solution was determined by colorimetric analysis.

Tetraphenylarsonium nitrate

This reagent was prepared by dissolving the chloride salt, obtained from the Hach Chemical Company of Ames, Iowa, in water and passing the resulting solution through the anion exchange resin Dowex-1. The resin was previously converted to the nitrate form by charging it with nitric acid.

Counting Method

Preparation of samples for counting

It was usually most convenient to count samples in the form of manganese dioxide precipitates. In experiments involving the manganese (II)-permanganate...
Manganese dioxide precipitates were obtained either directly from the reaction mixtures as a result of the reaction between manganese (II) and permanganate or by means of the oxidation of manganese (II) to manganese dioxide. These latter oxidations were carried out with sodium bromate in sulfuric acid solution. Koltchoff and Sandell (33) have reported that oxidation of manganese (II) with sodium bromate unavoidably produces some permanganate. A few exploratory experiments, however, have shown the amount of permanganate formed from solutions one normal in sulfuric acid may be considered negligible.

Samples for counting were obtained by collecting precipitates on washed, dried, and weighed discs of Whatman #50 filter paper. For this procedure standard sintered glass, chimney-type filters were employed. Manganese dioxide samples were washed with water followed by alcohol and ether and then dried in an oven at approximately 60° C. Samples of tetraphenylarsonium permanganate were washed with water only and then dried in air due to the solubility of this salt in alcohol.

For counting, all samples were mounted on cardboard squares and covered with a small piece of cellophane 3.5 mg/cm² in thickness. These mountings were in turn attached to metal shields by means of scotch tape for insertion into the counter housing. By this method it was possible to accurately reproduce the counting geometry for all samples counted.

**Counting of samples**

Since the active manganese used in these experiments is characterized by X-rays and gamma radiation, all counting was done with a Model TJC 3A end window Geiger Mueller tube manufactured by Tracerlab, Inc. of Boston, Massachusetts. This type of tube employs a gas mixture containing argon and thus possesses a higher efficiency for electromagnetic radiation than does the standard G-M tube. The mica window thickness was given as 1.8 mg/cm². A model 165 scaling unit manufactured by Nuclear Instruments Chemical Corporation was used in conjunction with the Geiger tube. In order to reduce the background count, a standard cast iron housing was employed. This was equipped with a sample holder which further insured reproducible geometry and located the sample about one centimeter from the mica window.

**Correction of counting data**

A number of corrections were applied to the observed counting data. The usual procedures for background and decay corrections were followed and, in addition, a correction for self-scattering in the sample was
employed. In order to obtain the scattering factor, several samples of manganese dioxide having varying thicknesses were prepared. Since all of these samples were known to have identical specific activities, disintegrations/min. mg., a plot of sample thickness versus observed specific activity, counts/min. mg., resulted in a curve which could be used in correcting all subsequent sample activities to the same thickness. The curve obtained is reproduced in Figure 1.

Analyses

Colorimetric analysis

With the exception of standardization of permanganate solutions against sodium oxalate, all manganese determinations were made by the colorimetric method. Of the several well established procedures available for the oxidation of manganese to permanganate, the periodate method was chosen mainly for its convenience. Since an excellent discussion of this method may be found in a pamphlet by G. F. Smith (34), no mention will be made here of the details of the procedure.

In making color intensity comparisons, a Beckman model D. H. spectrophotometer was used throughout. This instrument, manufactured by Beckman Instruments, Inc. of South Pasadena, California, employs a quartz prism together with a tungsten filament light source and a cesium-antimony phototube for use primarily below 620 millimicrons. As is well known, the absorption spectrum of permanganate contains twin peaks at wave lengths of approximately 525 and 585 millimicrons. At these wave lengths, therefore, the instrument is most sensitive to small changes in the permanganate concentration. A wavelength of 525 millimicrons was chosen for all absorbancy measurements.

Analysis of tetraphenylarsonium precipitates

The analysis of these precipitates for their manganese content was complicated by the fact that they were mixtures of the perchlorate and permanganate salts. In addition, the presence of the tetraphenylarsonium ion in a solution makes colorimetric analysis by periodate oxidation impossible due to the insolubility of tetraphenylarsonium periodate. In view of these difficulties, the following procedure was adopted for the analysis. Solution of the samples was effected by warming in a fifty per cent alcohol solution. This treatment also conveniently brought about the reduction of the permanganate ion to manganese (IV) which was in turn further reduced to manganese (II) by the addition of a small amount of acidified hydrogen peroxide. Evaporation of the solution together with the addition of a few drops of perchloric acid resulted in the recrystallization of the tetraphenylarsonium perchlorate precipitate.
Figure 1. Self-scattering in manganese dioxide precipitates.
Filtration of the solution thus removed the objectionable tetraphenylarsenonium ion leaving the manganese (II) in the filtrate ready for periodate oxidation to permanganate. It was necessary, of course, to first remove the excess of peroxide present by boiling the solution. Colorimetric analysis was then completed using the spectrophotometer.

PROCEDURE AND RESULTS

Manganese (II) -- Manganese Dioxide Exchange

Although this exchange has been studied by several investigators, in general, the conditions under which their experiments were performed did not closely parallel those existing in a Guyard mixture. In the present studies, the following procedure was employed. Manganese dioxide was prepared by mixing appropriate amounts of inactive manganese (II) perchlorate, potassium permanganate and perchloric acid. The concentrations employed were chosen to allow complete reduction of the permanganate in less than one minute leaving a small excess of manganese (II). Visual observations on such a mixture indicated that the manganese dioxide when first formed was quite finely divided. Over a period of two minutes, however, it assumed a more granular form, the color change being from a chocolate brown to a brown black. Following this period very little change was visible in the degree of dispersion of the precipitate. Two minutes after the mixing of permanganate and manganese (II) the exchange reaction was initiated by the rapid addition of active manganese (II). The resulting mixture was allowed to remain intact for the desired exchange period and then it was centrifuged and the manganese dioxide collected on a filter paper disc. The excess permanganate (II) in the filtrate was oxidized to manganese dioxide and also collected.

The precipitates were counted and analyzed for their manganese content. From the data obtained, the fraction of exchange, as defined by

\[ F = \frac{S_{\text{obs}} - S_0}{S_{100} - S_0} \]

was calculated. "Sobs" refers to the observed and specific activity in counts/min. mgMn. while "S100" and "S0" represent the specific activities expected for one hundred per cent and zero per cent exchange respectively. In these calculations "S100" was obtained by dividing the total activity added by the total milligrams of manganese present in all forms. "S0" would obviously be 0 for the precipitate. For the excess manganese (II), however, it would be equal to the quotient of the total activity divided by the total milligrams of manganese (II) found in the filtrate. The data and results are given in Table II under experiments 1, 2, and 3.
In order to determine the effect of aging on the amount of exchange observed, experiments 4 and 5 of Table 2 were carried out. These experiments differ from experiments 1, 2, and 3 only in the time of addition of active manganese (II) and in the length of the exchange period. In experiment 4, active manganese was added to the solution containing manganese dioxide one minute after the mixing of permanganate and manganese (II) to form the precipitate. At this point the manganese dioxide was light in color and apparently finely divided. In experiment 5, however, the precipitate was allowed to age 25 minutes before the addition of active manganese (II). During this time the manganese dioxide had darkened in color to almost black and had become quite granular. In both experiments the length of the exchange period was two minutes, after which, the precipitate was centrifuged off and collected. The calculations of fraction of exchange were again based on equation (21) and are summarized in Table 2.

Exchange in the Guyard Reaction

Previous investigators have in several cases carried out exchange studies on systems involving pairs of the oxidation states of manganese suspected of taking part in the Guyard reaction. It was felt, however, that an experiment which actually measured the exchange occurring during the course of the reaction would be of value. The experiment carried out was following: A suitable amount of standard potassium permanganate was added to a perchloric acid solution of tagged manganese (II) perchlorate. The manganese (II) was in approximately a two-fold excess. By varying the concentration of perchloric acid in the solution it was possible to vary the total reaction time as desired. In experiments 6 and 7 the formation of manganese dioxide occurred within one or two minutes, while in experiment 8 the formation of the precipitate was more gradual. Upon completion of the reaction, the manganese dioxide which had formed was removed from the solution by centrifugation and the separation completed by passing the centrifugate through a disc of Whatman #50 filter paper. The manganese dioxide in the centrifuge tube was then slurried and collected on the same filter paper, and after thorough washing and drying, its specific activity was determined from its counting rate and its manganese analysis. The excess manganese (II) in the filtrate was oxidized to manganese dioxide and its specific activity also determined in each experiment. Total reaction times were estimated to be three and sixteen minutes with reaction time being measured from the addition of manganese (II) to the disappearance of the last apparent trace of permanganate color.

The amount of exchange which had occurred was calculated in the following manner, employing the definition of fraction of exchange given by equation (21): "$S_{100}$" was again given by the quotient of the total activity observed divided by the total milligrams of manganese present in all forms. "$S_{0}$" for the unreacted manganese (II) was also easily obtained since it would be equal
### Table 2

Data and results of experiments on the exchange between manganese (II) and manganese dioxide at room temperature.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time after mixing Tracer added (min.)</th>
<th>Volume of solution (ml.)</th>
<th>Conc. HClO₄ x 10⁻³ (moles/liter)</th>
<th>Conc. SO₄⁻⁻ x 10⁻⁴ (mg.)</th>
<th>Wt. Mn added with MnII (mg.)</th>
<th>Wt. of Mn recovered in MnII (mg.)</th>
<th>Wt. of Mn recovered in MnO₂ (mg.)</th>
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<tbody>
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<td>#1</td>
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<td>206</td>
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<td>19.36</td>
<td>9.05</td>
<td>18.03</td>
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<td>0</td>
<td>19.36</td>
<td>9.05</td>
<td>18.24</td>
</tr>
<tr>
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<td>0</td>
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<td>9.05</td>
<td>18.24</td>
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<td>4.56</td>
<td>17.46</td>
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<td>1.56</td>
<td>23.00</td>
<td>4.56</td>
<td>17.46</td>
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<table>
<thead>
<tr>
<th>Experiment</th>
<th>Activity found in MnII (cts./min.)</th>
<th>Activity found in MnO₂ (cts./min.)</th>
<th>Specific activities of MnII of MnO₂</th>
<th>Exchange Fraction</th>
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</thead>
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<td>7.95 5.01 9.57</td>
<td>1.74 5.01 0</td>
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<td>29.2</td>
<td>8.31 5.24 9.90</td>
<td>1.79 5.24 0</td>
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<tr>
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<td>26.8</td>
<td>8.15 5.07 9.62</td>
<td>1.63 5.07 0</td>
</tr>
<tr>
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<td>427</td>
<td>97.6</td>
<td>24.16 15.78 30.05</td>
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<tr>
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<td>457</td>
<td>70.3</td>
<td>26.19 15.78 30.21</td>
<td>4.45 15.78 0</td>
</tr>
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</table>
to the specific activity of the original manganese (II) perchlorate stock solution. "Sn" for the manganese dioxide precipitate, however, was dependent on the quantity of the original manganese (II) found in the final precipitate. This quantity was not obtained from the stoichiometry of equation (1) since in the presence of excess manganese (II) this stoichiometry was not observed. In practice, the amount of the original manganese (II) found in the precipitate was calculated by taking the difference between the total milligrams of manganese found in the manganese (II) fraction and the total milligrams of manganese added as manganese (II). The experiments together with the results have been summarized in Table 3.

Manganese (II) -- Permanganate Exchange

In the method used by Polissar (22) and Adamson (24) in their study of this exchange, the separation process involved the precipitation of manganese dioxide from the exchange system. The filtration of such systems may fail to completely remove manganese dioxide present. Although very little zero time exchange was found in their experiments, it was decided to investigate the exchange using a different method of separation. In the procedure adopted in this study, solid manganese dioxide does not appear.

Several methods were tested for the separation of the two exchanging species. Some extraction and exchange column techniques proved unsatisfactory. It was possible, however, to separate the permanganate from the solutions by precipitating it with tetraphenylarsonium nitrate reagent. Since the perchloric ion is also precipitated by this reagent, it was impossible to investigate the exchange in perchloric acid solution by this method. Separations in nitric acid solution were, however, very clean. As a result, the possibility of carrying out the exchange experiments in nitric acid solutions was investigated.

Visual observations on mixtures of manganese (II), permanganate, and nitric acid showed that by working in solutions approximately $10^{-4}$ molar in permanganate and manganese (II) and 2 normal in nitric acid, the appearance of manganese dioxide could be delayed for periods up to approximately seven hours. A spectrophotometric investigation of such a mixture, described in a later section, failed to indicate any large difference between the behavior of perchloric acid solutions and nitric acid solutions. In view of these results the following method was adopted for the exchange studies: An appropriate amount of standard potassium permanganate was added to a solution of active manganese (II) perchlorate containing enough nitric acid to delay the appearance of manganese dioxide for at least four hours. The beaker containing the reaction mixture was at once covered and placed in a constant temperature bath regulated at $25 \pm .1^\circ C$. At desired time intervals, aliquots of the exchange system were withdrawn and immediately added with stirring to solutions of tetraphenylarsonium nitrate. Easily filterable precipitates
Data and results of experiments on the exchange occurring during the course of the Guyard reaction at 25°C

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time after mixing, MnO₂ separated (min.)</th>
<th>Volume of solution (ml.)</th>
<th>Conc. Mn II x 10⁴ (mole/liter)</th>
<th>Conc. MnO₄⁻ x 10⁴ (mole/liter)</th>
<th>Conc. HClO₄ (mg.)</th>
<th>Wt. of Mn Added as Mn II (mg.)</th>
<th>Wt. of Mn Added as MnO₄⁻ (mg.)</th>
<th>Wt. of Mn Recovered as Mn II (mg.)</th>
<th>Wt. of Mn Recovered as MnO₂ (mg.)</th>
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<td>3</td>
<td>212</td>
<td>12.75</td>
<td>5.31</td>
<td>0.028</td>
<td>14.85</td>
<td>6.19</td>
<td>4.43</td>
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<tr>
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<td>220</td>
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<td>5.12</td>
<td>0.027</td>
<td>14.85</td>
<td>6.19</td>
<td>4.40</td>
<td>16.42</td>
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<td>#8</td>
<td>10</td>
<td>210</td>
<td>12.87</td>
<td>5.36</td>
<td>0.057</td>
<td>14.85</td>
<td>6.19</td>
<td>4.74</td>
<td>16.22</td>
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</table>

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Activity found in Mn II (cts./min.)</th>
<th>Activity found in MnO₂ (cts./min.)</th>
<th>Specific Activities of Mn II</th>
<th>Specific Activities of MnO₂</th>
<th>Fraction exchange</th>
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<tr>
<td></td>
<td>S₀obs</td>
<td>S₁₀₀</td>
<td>S₀</td>
<td>S₀</td>
<td>F (%)</td>
</tr>
<tr>
<td>#6</td>
<td>917 ± 3</td>
<td>3401 ± 10</td>
<td>207.0</td>
<td>205.7</td>
<td>290.8</td>
</tr>
<tr>
<td>#7</td>
<td>938 ± 3</td>
<td>3374 ± 10</td>
<td>213.2</td>
<td>207.1</td>
<td>290.4</td>
</tr>
<tr>
<td>#8</td>
<td>973 ± 4</td>
<td>3278 ± 10</td>
<td>205.3</td>
<td>202.8</td>
<td>286.3</td>
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</table>
composed of the perchlorate and permanganate salts of the tetraphenylarsenium ion formed in a few seconds. After allowing three minutes for maximum precipitation of the permanganate, the precipitates were filtered off, washed with water and allowed to dry in air. The specific activity of the samples was then determined.

Experiments on the precipitation of permanganate from mixtures such as the ones encountered in these experiments indicated that precipitation was not complete. Furthermore, the amount of permanganate precipitated decreased as the excess of tetraphenylarsenium nitrate reagent was increased. As a result the amount of this reagent used was kept to a minimum.

The fraction of exchange which had occurred was again calculated from equation (21). Since all of the activity was added as manganese (II), "S0" for the permanganate precipitate would of course be zero. On the other hand, for complete exchange, "S100" would again be calculated from the total activity added and the total milligrams of manganese present in all forms. The exchange experiments together with the results are given in Table 4.

In the treatment of counting data for the manganese (II) -- permanganate exchange, some difficulty was encountered because of the low counting rates obtained. Consequently, it was necessary to count both samples and background for long periods in order to obtain statistically reliable results. The true counting rate of a sample was obtained by weighing individual rates by the reciprocal of the square of the standard deviation and combining them by means of the equation,

\[ R_{\text{true}} = \frac{1}{\frac{1}{\sigma_i^2}} \left[ \frac{1}{\sigma_i^2} R_i \right] \pm \frac{1}{\sqrt{\frac{1}{\sigma_i^2}}} \]

Spectrophotometric Examination of Guyard Mixtures

It may be seen from the data of the manganese (II) -- permanganate exchange that the amount of permanganate precipitated by the tetraphenylarsenium ion generally decreased with an increase in the time of contact of manganese (II) and permanganate. This was taken to be indicative of the existence of a reacting system rather than a system in which no appreciable chemical change occurs before the formation of solid manganese dioxide. Since the permanganate ion is so well adaptable to colorimetric methods, it was decided that any change in the manganese (II) -- permanganate system could most easily be detected by following the optical density \(^3\) of such a mixture.

The optical density of a solution was taken as

\[ O.D. = \log_{10} \frac{I_0}{I} \]

where I and I\(_0\) are the intensities of the light transmitted by the sample and by the pure solvent, respectively. The molar extinction coefficient, \(\varepsilon\), which is useful for indicating the absorption of the solute, was determined by

\[ O.D. = \varepsilon bc \]

in which b is the light path in cm. and c is the concentration in moles/liter.
Table 4

Data and results of experiments on the manganese (II) -- permanganate exchange at 25°C

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<td></td>
<td>x10⁴</td>
<td></td>
<td>x10⁴</td>
<td></td>
<td>(moles/liter)</td>
<td>time</td>
<td>(mg.)</td>
<td>(cts./min.)</td>
<td>(cts./min.mg.Mn)</td>
<td>(%)</td>
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<td>11.71</td>
<td>122.33</td>
<td>0.96±.30</td>
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<td>2 /2</td>
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<td>121.80</td>
<td>0.20±.25</td>
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<td>19.14</td>
<td>120.47</td>
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<td>5.13</td>
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<td>124.49</td>
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at a wave length of 525 millimicrons at which the spectrophotometer is most sensitive to changes in the permanganate concentration. The composition of the solutions investigated by means of the spectrophotometer are given in Table 5.

The procedure employed was the following: The required amount of permanganate was added to the other constituents of a typical reaction mixture to initiate the reaction. The resulting solution was stirred briefly, and a sample was poured into one of the centimeter cells of the spectrophotometer. Since the machine had been previously prepared for use, an initial reading of the optical density could be obtained within a few minutes. Thereafter, optical density readings were taken at frequent intervals for periods up to ten hours. The temperature of the reaction mixture was conveniently maintained constant by means of a constant temperature bath in conjunction with a Sargent thermoregulator and automatic heating assembly. Water from the bath was circulated around the chamber containing the reaction mixture cells by means of a circulating pump operated from a variac at a suitable speed.

Since the optical density of the solution may be taken as proportional to the maximum amount of permanganate in the solutions, a plot of the logarithm of the optical density versus time gives a measure of the maximum permanganate order of the initial manganese (II) -- permanganate reaction. Manganese (II) was considered to be present in large excess. These graphs together with linear plots were made and are reproduced in Figures 2 and 3. From the fact that log O. D. versus time is straight within the experimental error, it was concluded that the reaction is first order in permanganate. Although permanganate solutions themselves appear to be unstable in acid solution, Figure 4, the rate of the disappearance of permanganate was much greater in the presence of manganese (II).

Rate of Manganese (II) -- Permanganate Exchange

Since it was shown that permanganate disappears from the exchange mixtures at a measurable rate, this phenomenon should be included in the consideration of the rate of exchange. If it is assumed that reactions (24) and (25) take place at rates "R₁" and "R₂",

(24) \[ *\text{Mn}^{++} + \text{MnO}_4^- \rightarrow \text{Mn}^{++} + *\text{MnO}_4^- \] rate = R₁

(25) \[ \text{Mn}^{++} + \text{MnO}_4^- \rightarrow \text{Products} \] rate = R₂

then "R₂" may be set equal to the rate of the disappearance of permanganate, i.e.,

(26) \[ R₂ = - \frac{d (\text{MnO}_4^-)}{dt} \]

where parentheses correspond to molar concentrations.
Table 5

Composition of solutions investigated spectrophotometrically at 25°C.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$[\text{Mn}^{II}]$</th>
<th>$[\text{MnO}_4^-]$</th>
<th>$[\text{HNO}_3]$</th>
<th>$[\text{HClO}_4]$</th>
<th>Total volume</th>
<th>Reaction half-time (hrs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#12</td>
<td>0</td>
<td>$3.5 \times 10^{-4} \text{M}$</td>
<td>2.0N</td>
<td>0</td>
<td>105 ml.</td>
<td>49</td>
</tr>
<tr>
<td>#13</td>
<td>0</td>
<td>$3.5 \times 10^{-4} \text{M}$</td>
<td>0</td>
<td>2.0N</td>
<td>105 ml.</td>
<td>29</td>
</tr>
<tr>
<td>#14</td>
<td>$8.7 \times 10^{-4} \text{M}$</td>
<td>$3.5 \times 10^{-4} \text{M}$</td>
<td>0</td>
<td>2.0N</td>
<td>105 ml.</td>
<td>12</td>
</tr>
<tr>
<td>#15</td>
<td>$8.7 \times 10^{-4} \text{M}$</td>
<td>$3.5 \times 10^{-4} \text{M}$</td>
<td>2.0N</td>
<td>0</td>
<td>105 ml.</td>
<td>12</td>
</tr>
</tbody>
</table>
Figure 2. Linear plot of optical density versus time mixtures of manganese (II) and permanganate in acid solution at 25°C.
Figure 3. Semilogarithmic plot of optical density versus time for mixtures of manganese (II) and permanganate in acid solution at 25°C.
Figure 4. Semilogarithmic plot of optical density versus time for acid solutions of permanganate at 25°C.
Also, if \( u \), the number of active manganese atoms present as permanganate per unit volume at any time, is given by

\[
(27) \quad u = SVII (\text{MnO}_4^-)
\]

where "S" represents the specific activity in counts/min. mg., then \( du \) is given by,

\[
(28) \quad \frac{du}{dt} = \frac{dSVII}{dt} (\text{MnO}_4^-) - R_2 SVII.
\]

From (24) and (25) \( \frac{du}{dt} \) may also be given by

\[
(29) \quad \frac{du}{dt} = R_1 (SII - SVII) - R_2 SVII.
\]

When the values of \( \frac{du}{dt} \) in equations (28) and (29) are set equal, it is found that

\[
(30) \quad \frac{dSVII}{dt} \frac{R_1}{(\text{MnO}_4^-)} (SII - SVII).
\]

Also, from the definition of "F" as given by equation (21), it is at once found that

\[
(31) \quad \log (1 - F) = \log (SVII - SVII) - \log SVII.
\]

Differentiation of \( \log (1 - F) \), considering \( SVII \) to be a constant, yields

\[
(32) \quad \frac{d\log(1 - F)}{dt} = -\frac{dSVII}{dt} \frac{1}{SVII - SVII}.
\]

If \( \frac{dSVII}{dt} \) is replaced by its value in equation 30, then

\[
(33) \quad \frac{R_1}{(\text{MnO}_4^-)} = -\frac{d\log(1 - F)SVII - SVII}{dt} SII - SVII
\]

and for \( t = 0 \),

\[
(34) \quad R_1^0 = -\frac{d\log(1 - F)}{dt} \frac{[\text{Mn}^{+2}]_o [\text{MnO}_4^-]_o}{[\text{Mn}^{+2}]_o + [\text{MnO}_4^-]_o}.
\]

Equation (34) has the same form as the exchange rate expression in a steady state system, i.e., one for which \( R_2 = 0 \). It gives the exchange rate, however, only for the time, \( t = 0 \), and in general the expression in equation (33) must be used. Insofar as the concentrations, and therefore \( R_1 \), change with time, the \( \log (1 - F) \) function would be expected to have curvature.

The accuracy of the data which were obtained for the initial portion of the exchange process was not sufficient to detect any deviation from linearity. Therefore, from the slopes determined from the least squares treatment of
the log (1 - F) function, Figures 5, 6, and 7, values of \( R_1^0 \) were calculated using the initial concentrations. A pure exchange half-time may be taken as

\[
(35) \quad T_{1/2}^R = \frac{\log e}{R_1^0} \frac{[\text{Mn}^{4+}]_0}{[\text{Mn}^{4+}]_0 + [\text{MnO}_4^-]_0}.
\]

However, a pure exponential form will not be obtained for (1 - F). The exchange rates and half-times obtained in this way have been listed in Table 6.

Table 6

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Half-time of exchange (hrs.)</th>
<th>Rate of exchange (moles/hrs.l)</th>
<th>Rate calculated from Adamson's (24) formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>#9</td>
<td>15</td>
<td>1.6 x 10^{-5}</td>
<td>1.8 x 10^{-5}</td>
</tr>
<tr>
<td>#10</td>
<td>9</td>
<td>2.0 x 10^{-5}</td>
<td>3.9 x 10^{-5}</td>
</tr>
<tr>
<td>#11</td>
<td>11</td>
<td>1.4 x 10^{-5}</td>
<td>2.5 x 10^{-5}</td>
</tr>
</tbody>
</table>

**DISCUSSION**

Manganese (II) -- Manganese Dioxide Exchange

From the data and results of Table II it was indicated that a rapid, partial exchange occurs between manganese (II) and manganese dioxide prepared by the reduction of permanganate with excess manganese (II) in acid solution. In experiments attempting to measure the exchange rate it was found that the major portion of the exchange occurred within the first one or two minutes of contact. Any further exchange was very slow. With a precipitate which had been allowed to age for twenty-five minutes, the amount of exchange observed was less than that found with precipitates used immediately after their formation.
Figure 5. Graph of manganese (II) -- permanganate exchange observed in experiment 9.
Figure 6. Graph of manganese (II) -- permanganate exchange observed in experiment 10.
Figure 7. Graph of manganese (II) permanganate exchange observed in experiment II.
Jordan (30) has suggested that the rapid exchange observed in his experiments may be interpreted as a rapid exchange between manganese (II) in the solution and manganese (II) contained in the precipitates. That the precipitates of manganese dioxide prepared with excess manganese (II) in acid solution do not contain only manganese (IV) is indicated by the observed stoichiometry of the reaction which is given by,

\[(\text{36}) \quad 1.68 \text{MnO}_4^- + 3 \text{Mn}^{++} \rightarrow 4.68 \text{MnO}_1.90 \cdot x \text{H}_2\text{O}.\]

Calculations have shown, however, that complete exchange between manganese (II) in solution and manganese of oxidation state lower than four contained in the precipitate could not produce the relatively high exchange observed in the present experiments.

It has been concluded that manganese in the interior of precipitate particles did not exchange with manganese (II) in the solution and that a rapid exchange took place on the surface layer. Such a process would lead to a rapidly established exchange equilibrium between the solution and manganese dioxide surface. Further exchange would be governed by the slow penetration of activity to the interior of manganese dioxide particles. Speculation as to the size of manganese dioxide particles necessary such that approximately thirty per cent of the manganese dioxide be on a surface has led to the belief that the precipitates consist of unusually small particles which loosely coalesce to produce fairly granular precipitates. Particles with thirty per cent of the manganese on the surface would contain about 8000 manganese atoms and be about 6 \(\mu\) in size. Since exchange results with a precipitate aged for twenty-five minutes did not differ to a large extent from those obtained with a precipitate freshly formed, it was concluded that the actual aging process is slow.

Results reported by several previous investigators indicating the absence of exchange between manganese (II) and manganese dioxide have, in several cases, been difficult to interpret since frequently exact experimental procedures have been omitted. It would appear, however, that the treatment of precipitates and method of preparation are of primary importance in determining the amount of exchange they will undergo when placed in contact with a solution of manganese (II).

The absence of exchange observed by Polissar (22) in an experiment similar to those described here may be a result of the experimental method used. He has employed a tagged precipitate prepared in the absence of excess manganese (II). It is possible that upon the addition of inactive manganese (II) to such a precipitate an immediate deposition of inactive manganese from the solution onto the precipitate occurred with a shielding of the tagged manganese in the interior of the particles from exchange.
Exchange in the Guyard Reaction

In experiments designed to measure the exchange taking place during the Guyard reaction, it was found that manganese (II) undergoes a rapid and complete exchange with manganese initially present as permanganate. Also, since a rapid exchange between manganese (II) and either permanganate or manganese (VI) need not be considered, it was concluded that the observed rapid exchange occurs between manganese (II) and some species of manganese (IV). The conditions under which the exchange takes place, however, were not at once apparent.

It may be shown that if the exchange process consisted of rapid and complete exchange between manganese (II) and the surface of manganese dioxide particles, the growth of the precipitate would have a net result of a concentration of active manganese in the interior of the particles. The precipitation process may be represented schematically by the expression,

$$\text{(37)} \quad (\alpha - 1) \text{MnO}_4^- + \text{Mn}^{2+} \rightarrow \text{intermediates} \rightarrow \alpha \text{Mn precipitate}.$$  

Consider the idealized case in which the "intermediates" of reaction (37) exchange completely with the manganese (II) present. Let:

- \((\star \text{Mn})\) = the number of active manganese atoms,
- \((\text{Mn})\) = the weight of manganese (mg).

Superscripts II and p indicate manganese present as the manganese (II) in solution and manganese in the precipitate, respectively. Subscripts, 0 and ∞ refer to zero and infinite time, respectively. From equation (37),

$$\text{(38)} \quad \alpha \frac{d}{dt} \text{(Mn}^{\text{II}}\text{)} = \frac{d}{dt} \text{(Mn}^{\text{P}}\text{)};$$

also it may be seen that

$$\text{(39)} \quad \frac{d}{dt} (\star \text{Mn}^{\text{II}}) = \frac{d}{dt} (\star \text{Mn}^{\text{P}}) = S^{\text{II}} \frac{d}{dt} \text{(Mn}^{\text{P}}\text{)} = -S^{\text{II}} \alpha \frac{d}{dt} \text{(Mn}^{\text{II}}\text{)}.$$  

or

$$\text{(40)} \quad d \log (\star \text{Mn}^{\text{II}}) = \alpha \frac{d}{dt} \log \text{(Mn}^{\text{II}}\text{)}.$$  

Upon integration equation (40) gives

$$\text{(41)} \quad \log \left(\frac{\star \text{Mn}^{\text{II}}}{\star \text{Mn}_0^{\text{II}}}\right) = \alpha \log \left(\frac{\text{Mn}^{\text{II}}}{\text{Mn}_0^{\text{II}}}\right)$$

or

$$\text{(42)} \quad S^{\text{II}} = S_0^{\text{II}} \left[\frac{\text{Mn}^{\text{II}}}{\text{Mn}_0^{\text{II}}}\right]^{-\alpha -1}$$
For the first reaction listed in Table III, for which \((\alpha - 1)\) is 0.595, a value of 145 is predicted for \(s^{III}\) by equation (42). In this case the per cent of exchange, calculated by

\[
(43) \quad \% \text{ Exchange} = 100 \frac{(S_o^{II} - S_{obs}^{II})}{(S_o^{II} - S_0^{II})},
\]

is 170 per cent. However, since the experiments in Table II showed that the surface of the precipitate subjects about forty per cent of the precipitated manganese to exchange, final values of \(s^{III} = 169\) and \(s^{P} = 215\) counts/min.mg. might be expected. It would thus seem that the observed results in which equal specific activities were observed for both precipitates and solution would not be consistent with a process involving the rapid growth of manganese dioxide particles.

In view of the foregoing, a process has been proposed which appears to resolve the above difficulties. It is first assumed that manganese (IV) in solution together with manganese on the surface of manganese dioxide particles undergo a rapid exchange with manganese (II) in solution. The assumption is also made that manganese dioxide particles grow only slowly in comparison to the rate of exchange and the duration of the manganese (II) -- permanganate reaction. It is felt that only by a mechanism such as this would it be possible to attain a state in which an exchange equilibrium might be reached involving essentially all manganese present in the system. It might be added that a distinction must here be made between the actual growth of a crystalline precipitate and the granulation of a precipitate due to the coalescence of small particles. It is believed that it is the latter process which is responsible for the formation of easily filterable precipitates of manganese dioxide.

**Manganese (II) -- Permanganate Exchange**

The slow apparent exchange observed between manganese (II) and permanganate in these experiments is in qualitative agreement with the results reported by Adamson (24). Table VI shows that the rate of exchange calculated from the equation he gave was somewhat greater than that calculated in the present experiments from equation (34).

By considering the hitherto neglected slow reaction between manganese (II) and permanganate, a process may be derived by which exchange might appear to take place. Since a precipitate of manganese dioxide is not observed for a period of hours although it has been shown that permanganate and manganese (II) undergo a significant reaction, it was concluded that the concentration of some product species, presumably a kinetically inert hydrolysis polymer of manganese (IV), increased in the solution with time. The simultaneous precipitation of this species with tetraphenylarsonium permanganate or the precipitation of the species on these precipitates would also result
in the appearance of activity in the samples obtained. In addition, with an increase in time, an increase in the amount of activity precipitated might be expected because of further progress in the slow reduction of permanganate. The results of Adamson (24) would be interpreted as a failure to precipitate the above-mentioned species as manganese dioxide by the rapid neutralization of the Guyard mixture.

In view of the above, it is felt that an exchange mechanism involving a slow electron exchange between the two products of the reaction,

\[ 3 \text{Mn}^{II} + \text{MnO}_4^- \leftrightarrow 3 \text{Mn}^{III} + \text{Mn}^{IV} \]

would not appear to be required.

**Spectrophotometric Investigation**

From experiments measuring the continuous disappearance of permanganate from mixtures of manganese (II) and permanganate several indications have been obtained concerning the mechanism of the Guyard reaction. The lack of any significant autocatalysis in the reaction prior to the sudden formation of manganese dioxide may be taken as evidence that a supersaturation of the solution with manganese (IV) occurs before precipitation. It would also appear that the products of the initial manganese (II) - permanganate reaction do not react rapidly with the permanganate present, at least in the absence of solid manganese dioxide.

Since an experimental curve of the change in permanganate concentration with time has been obtained, some kinetics calculations were carried out in an attempt to determine whether or not the data was consistent with a mechanism given by

\[ \text{(20)} \quad \text{Mn}^{II} + \text{MnO}_4^- \leftrightarrow \text{Mn}^{III} + \text{Mn}^{VI} \quad K_{\text{eq}} = K_1 \]

\[ \text{(14)} \quad \text{Mn}^{III} + \text{Mn}^{VI} \rightarrow 2 \text{Mn}^{IV} \quad \text{Rate} = R_1 \]

\[ \text{(15)} \quad \text{Mn}^{II} + \text{Mn}^{IV} \leftrightarrow 2 \text{Mn}^{III} \quad K_{\text{eq}} = K_2 \]

The calculations were the following: Consider manganese (II) to be present in large excess. Let:

\[ a = \text{The initial concentration of permanganate} \]

\[ y = \text{The concentration of permanganate at any time, } t. \]

From equations (20) and (14) it may be seen that
(45) \[ \frac{dy}{dt} = k (MnII) (MnVI). \]

Also the equilibrium expressions for reactions (20) and (15) may be combined to give

\[ (46) \quad (MnVI) = \frac{(MnII)^{1/2} (MnO_4^-) K_1}{(MnIV)^{1/2} K_2^{1/2}}; \]

or, since MnIV = 5/2 (a - y),

\[ (47) \quad (MnVI) = \frac{(MnII)^{1/2} y K_1}{(5/2)^{1/2} (a - y)^{1/2} K_2^{1/2}}. \]

When the value of (MnVI) given by equation (47) is substituted into equation (45) it is found that

\[ (48) \quad \frac{dy}{dt} = k (MnII)^{3/2} \frac{y K_1}{(5/2)^{1/2} (a - y)^{1/2} K_2^{1/2}}. \]

In MnII is present in large excess and if K_2 << 1, then

\[ (49) \quad \frac{dy}{dt} = k' \frac{y}{(a - y)^{1/2}}. \]

Integration of equation (49) between the limits y = a and y = y gives upon simplification

\[ (50) \quad \sqrt{1 + y/a} + \log_e \frac{1 + \sqrt{1 - y/a}}{\sqrt{y/a}} = k'' t. \]

Upon inspection it is seen that a straight line would be expected when the function of permanganate concentration given by the left side of equation (50) is plotted versus time. This graph is given in figure 8. Values of y/a together with the corresponding values of t were obtained from the experimental perchloric acid curve of figure 2. From the fact that the curve obtained was by no means straight it was concluded that under the existing conditions the reaction mechanism represented by equations (20), (44) and (15) was not important in the course of this reaction.

On the other hand the data would appear to be consistent with a mechanism, supported by Malcolm and Noyes (35) of the following type:

\[ (51) \quad Mn^{II} + MnO_4^- \rightarrow Mn^{III} + Mn^{VI} \text{ (rate controlling)} \]

\[ (44) \quad Mn^{VI} + Mn^{II} \rightarrow 2 Mn^{IV} \]

\[ (15) \quad Mn^{II} + Mn^{IV} \leftrightarrow 2 Mn^{III} \text{ (rapid)}. \]
Figure 8. Graph of equation (50) using experimental values of $y/a$ and $t$. 
Although it has not been demonstrated directly in the experiments of this paper that a rapid manganese (II) -- manganese (IV) exchange occurs in solution, it is felt that this exchange is rapid even in the absence of a manganese dioxide surface. An exchange mechanism represented by the disproportion reaction

\[
\text{Mn}^{II} + \text{Mn}^{IV} \leftrightarrow 2 \text{Mn}^{III}
\]

would not be contradictory to the data obtained.

**SUMMARY**

Radioactive manganese has been used in investigating several isotopic exchange reactions of manganese. A rapid partial exchange has been found to occur between manganese (II) and manganese dioxide prepared in excess manganese (II). It was indicated that only manganese on the surface of manganese dioxide particles takes part in the exchange. A complete and rapid exchange has also been found to occur during the course of the Guyard reaction. A rapid manganese (II) -- manganese (IV) exchange has been proposed as a probable mechanism. It is believed that the slow exchange observed between manganese (II) and permanganate is not a true exchange but is due to a carrying of active manganese by tetraphenylarsonium permanganate precipitates. A spectrophotometric examination of manganese (II) -- permanganate mixtures has provided an indication as to the mechanism of the initial reaction between manganese (II) and permanganate in acid solution.

**LITERATURE CITED**

19. Oberhauser, F., and Hensgner, W., Ber., 51, 521 (1928).


