temperature drops due to the cooling effect of the reaction must be guarded against. Using Benson's[10] method of calculating the average temperature drop across a reaction bulb and extending the treatment in an obvious manner to cylinders, one finds the values in Table II. In the 14.5-liter bulb reactants were kept at such a low pressure that the temperature drop did not exceed 1°. However in the 2-liter flask the runs at high pressures and high temperature, Fig. 2, are severely distorted by this effect. For severe temperature gradients such as these, the treatment[11] is oversimplified, and for endothermic reactions it represents the worst possible temperature drop, rather than the expected actual one.

TABLE II

CALCULATED AVERAGE TEMPERATURE DROP IN REACTION BULBS DUE TO SELF-COOLING EFFECT OF ENDOTHERMIC REACTION

Reaction cell	$[HNO_3]$ mole/cc. × 10^8	T, °C.	Av. temp. drop, °C.
2-l. bulb	3	375	0.03
	30	375	3
	3	400	0.1
	30	400	10
	3	425	0.3
	30	425	30
14.5-l. bulb	2.15	400	0.4
2.5 cm. dia. cylinder	100	395	2
	100	475	60

The last two entries are based on Frejacques' values, pp. 49–50 in ref. 4. Reactant pressures were chosen so high that very severe temperature drops occurred even in the small cylinders. This effect of self-cooling is believed to account for the remaining disagreement between our work and Frejacques, especially his low energy of activation.

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STANFORD, CAL.

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[10] S. W. Benson, *J. Chem. Phys.*, **22**, 46 (1954).

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Isotopic Exchange of Manganese during the Reaction between Manganese(II) and Permanganate[1,2]

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Isotopic exchange experiments with Mn^{54} have been performed which involved various chemical forms of manganese existing during the reaction of Mn^{++} with MnO_4^- in acid solutions to give a hydrous oxide containing manganese(IV). A rapid 30 to 40% exchange occurred between Mn^{++} and a freshly formed precipitate. However, 60–70% of the precipitate was unavailable for rapid exchange within 1 to 2 minutes of formation. Isotopic equilibrium during the over-all reaction between Mn^{+++} and MnO_4^- required that MnO_4^- be completely reduced to Mn^{IV} before the formation or growth of precipitate grains. Tetraphenylarsonium permanganate was precipitated from solutions of MnO_4^- and Mn^{+++} in 1 to 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 10 to 15 hours. Spectrophotometric studies showed that before a precipitate appeared at least 40% 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^{++} may not be real.

Introduction

The rate and the products of the reaction between manganese(II) and permanganate in aqueous solutions are strongly influenced by the content of the solution. Noyes[3] has reviewed the abundant evidence that in the familiar oxalate reduction of MnO_4^-, Mn^{++} effects an initial rapid reduction of the MnO_4^- to oxalato-complexes of Mn^{III} which slowly yield the products. In the autocatalytic periodate oxidation of Mn^{++}, Waterbury, Hayes and Martin[4] showed that MnO_4^- oxidizes Mn^{++} to iodato complexes of Mn^{III} which are in turn oxidized by periodate. However, in the presence of only dilute nitric or perchloric acids Mn^{++} reduces MnO_4^- to form a hydrous oxide precipitate containing Mn^{IV}. The reaction between these ions in homogeneous solutions is very slow. Tompkins[5] demonstrated quantitatively the autocatalytic nature of the formation of the precipitate. This reaction has been named the Guyard Reaction for which the equation is frequently written

$$3Mn^{++} + 2MnO_4^- + 2H_2O \longrightarrow 5MnO_2 + 4H^+ \quad (1)$$

In excess MnO_4^- the MnO_4^-/Mn^{++} ratio to react is $^2/_3$; however, the indefinite nature of the precipitate is in part indicated by ratios as low as 0.56 which are commonly observed in excess Mn^{++}. Freshly formed precipitates are very finely dispersed, but in a few minutes their color darkens and they are separable by centrifugation and filtration.

The possibility of isotopic exchange between Mn^{++} and MnO_4^- was originally investigated by Polissar[6] who found that negligible exchange occurred at room temperature in the 15 minutes before

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[1] Work was performed in the Ames Laboratory of the United States Atomic Energy Commission.

[2] Presented before the Division of Physical and Inorganic Chemistry at the 127th National Meeting of the American Chemical Society, Cincinnati, Ohio, April 4, 1955.

[3] R. M. Noyes, *Transactions N. Y. Acad. Sci.*, **13**, 314 (1951).

[4] G. R. Waterbury, A. M. Hayes and D. S. Martin, Jr., THIS JOURNAL, **74**, 15 (1952).

[5] F. C. Tompkins, *Trans. Faraday Soc.*, **38**, 131 (1942).

[6] M. J. Polissar, THIS JOURNAL, **58**, 1372 (1936).

a precipitate was discernible. The possibility of a rapidly established equilibrium

$$3Mn^{++} + 2MnO_4^- \rightleftarrows 5Mn^{IV} \qquad (2)$$

was therefore excluded as a possible step in the reduction of MnO_4^- by Mn^{++}. However, there might exist equilibria such as

$$3Mn^{++} + MnO_4^- \rightleftarrows 3Mn^{III} + Mn^{IV} \qquad (3)$$

or

$$Mn^{++} + MnO_4^- \rightleftarrows Mn^{III} + MnO_4^= \qquad (4)$$

if exchange between the products were slow.

Adamson[7] noted that in 2–3 molar $HClO_4$ the appearance of a precipitate was delayed several hours. For these solutions he reported a measurable exchange process

$$Mn^{*++} + MnO_4^- \longrightarrow Mn^{++} + Mn^*O_4^- \qquad (5)$$

for which the rate at 25° was given as

$$R = k_1(Mn^{++})^{4/3}(MnO_4^-)^{1/3}(H^+)^{4/3} \qquad (6)$$

where $k_1 = 2.6$ l.^{2}/moles^2 hr. He proposed that the equilibrium 3 was established and that the rate determining step was the reaction

$$Mn^{*III} + Mn^{IV} \longrightarrow Mn^{III} + Mn^{*IV} \qquad (7)$$

Adamson tagged the Mn^{++} and worked with an excess of MnO_4^-. He terminated the exchange by neutralizing the acid to give rapid precipitation. The excess permanganate was then reduced and collected as a counting sample. In the present work it was desired to utilize an alternative separation procedure. Permanganate was precipitated from the exchange mixtures as the tetraphenylarsonium salt. However, since $(As(C_6H_5)_4)ClO_4$ is insoluble, the exchange was followed in 1–2 *M* HNO_3 solutions instead of $HClO_4$.

Experiments have also been undertaken in an effort to clarify conflicting reports regarding the isotopic exchange between Mn^{++} and the hydrous oxides containing Mn^{IV} at room temperature. Polissar[6] found less than 5% exchange in 2 min. with a freshly formed precipitate. With a colloidal MnO_2 Libby[8] reported one result of 30 ± 20% exchange in 67 hours. On the other hand, Pullman and Haissinsky[9] reported 39% exchange for a Guyard precipitate in 15 minutes at 25°, a rapid complete exchange at 100°, and considerably different results with precipitates formed by other reactions. Most observers have agreed that well dried and aged preparations exchange only slowly at room temperature. It is apparently important in reporting such experiments to describe all conditions carefully.

In the present experiments exchange has been measured between Mn^{++} and the Mn^{IV} containing precipitates within a few minutes of their formation by the Guyard reaction. The exchange between Mn^{++} and Mn from the MnO_4^- during the course of the complete Guyard reaction was also determined.

Experimental

Materials and Analyses.—Reagent grade acids and chemicals meeting A. C. S. specifications were employed. Distilled water, redistilled from alkaline permanganate, was used to prepare solutions. $KMnO_4$ solutions were heated for one hour below the boiling point. After standing, they were filtered through glass sinters, diluted and standardized by oxalate titrations. The standardized $KMnO_4$ solutions were used to calibrate a periodate colorimetric procedure by which all other manganese fractions were analyzed. Aliquots of the $KMnO_4$ solutions were reduced and carried through the complete colorimetric procedure. A Beckman model DU spectrophotometer served for the experiments and assays. Manganese(IV) oxide precipitates were reduced by acid–H_2O_2 solutions before analyses. Mixed tetraphenylarsonium permanganate and perchlorate precipitates were dissolved in alcohol and a small amount of H_2O_2 added to complete the reduction to Mn^{++}. After evaporation, a small amount of $HClO_4$ was added to completely precipitate the $As(C_6H_5)_4^+$. Manganese was not detected in these precipitates and the filtrate was analyzed by the colorimetric procedure.

Radioactive Mn^{54}.—Mn^{54} was obtained by the (d,p2n) process from a cyclotron bombardment of Mn metal by *ca.* 80 Mev. deuterons. To remove radioactive impurities, carriers of Y, Ca, V, Ti, Cr and Fe were added and repeatedly separated from the Mn. A basic acetate separation of Fe^{III} was performed three times and finally MnO_2 was precipitated from acid solution by bromate oxidation. A stock $Mn(ClO_4)_2$ solution was prepared by dissolving the MnO_2 in a dilute $HClO_4$ by H_2O_2 reduction. Excess H_2O_2 was destroyed by heating in contact with platinum black.

All counting samples were collected as precipitates on a filter paper supported on a glass sinter in a chimney-type suction filter. Precipitates were mounted in a reproducible fashion on a cardboard backing with a Cellophane cover for counting. An end-window Geiger–Mueller counter model TGC-3A of Tracerlab, Inc., with high efficiency for X-rays was employed. Since the principal radiation was Cr–K X-rays, self-scattering effects were small and an empirical correction was readily made. Conventional corrections for decay were also employed.

Exchange between Mn^{++} and Freshly Formed Precipitates. Experiments 1.1 **and 1.2.**—To form a precipitate, 100.0 ml. of a solution which was 1.043×10^{-3} molar in $KMnO_4$ (5.73 mg. Mn) and 1.18×10^{-2} molar in $HClO_4$ was poured rapidly into a 100.0-ml. solution, 4.19×10^{-3} molar in $MnSO_4$ (23.0 mg. Mn), at 25 ± 1°. A precipitate was formed rapidly, and the pink color of permanganate was not discernible one minute after mixing. At a measured time after mixing 4.00 ml. of a 2.075×10^{-2} molar $Mn^*(ClO_4)_2$ (4.56 mg. Mn) solution was added. Two minutes later the mixture was transferred to centrifuge tubes and centrifuged for 5.0 min. The mixture was stirred vigorously by a magnetic stirrer from the time of mixing until they were transferred to the centrifuge tubes. In experiment 1.2 7 ml. of wash H_2O was employed to assist in the transfer of the precipitate. The samples were centrifuged for 5 minutes.

In experiments 1.3, 1.4 and 1.5, 100.0 ml. of a solution 1.059×10^{-3} molar in $KMnO_4$ (5.82 mg. Mn) was poured rapidly into 106.0 ml. of a solution which was 3.325×10^{-3} molar in $Mn(ClO_4)_2$ (19.36 mg. Mn) and 1.09×10^{-2} molar in $HClO_4$ at 25 ± 1° to form the precipitate. The mixture was stirred continuously with a magnetic stirrer. For the exchange 5 ml. of a solution which was 3.295×10^{-2} molar in $Mn^*(ClO_4)_2$ (9.05 mg. Mn) was added two minutes later. After different periods of contact the mixture was transferred to centrifuge tubes. The samples were centrifuged for 10 minutes.

Centrifuging in all the experiments yielded nearly clear centrifugates which were decanted into the chimney filter with a tared Whatman No. 50 paper and filtered under suction. The precipitate was then slurried and collected on the same filter paper. An initial H_2O wash was added to the filtrate. The precipitates were washed with alcohol and ether and dried in an oven at 60°. They were weighed for self-scattering corrections and mounted for counting. Manganese in the filtrates was oxidized by $NaBrO_3$ and the precipitates formed were filtered, washed and mounted in a similar fashion. After the counting rates were determined, each sample was dissolved in acidic H_2O_2 and the Mn-content determined colorimetrically for a check of the recovery. In this way the specific activity, S (cts./min. mg. Mn), of each fraction was determined and the fraction of exchange was calculated by the familiar expression

$$f = (S - S_0)/(S_\infty - S_0) \qquad (8)$$

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(7) A. W. Adamson, *J. Phys. Colloid Chem.*, **55**, 293 (1951).

(8) W. F. Libby, THIS JOURNAL, **62**, 1930 (1940).

(9) B. Pullman and M. Haissinsky, *J. phys. radium*, **8**, 36 (1947).

where S_∞ = total counts/total Mn and the subscript "0" indicates zero time. The results of these experiments are included in Table I.

TABLE I

EXCHANGE BETWEEN Mn^{II} AND FRESHLY PRECIPITATED MnO_2 AT 25°

Expt.	Time after mixing of Mn^{++} and MnO_4^-, min. Tracer added	Ppt. centri-fuged	Wt. Mn recovered As Mn^{++}, mg.	In ppt., mg.	(α − 1)	Specific activity, cts./min. mg. Mn In Mn^{++}	In ppt.	Fraction ex-change, %
1.1	1	3 to 8	17.5	15.8	0.57	24.5	6.18	39.2
1.3	2	7 to 17	18.2	16.4	.57	8.15	1.63	32.3
1.4	2	22 to 32	18.0	16.4	.57	7.95	1.73	34.8
1.5	2	32 to 42	18.2	16.3	.56	8.31	1.79	34.2
1.2	25	27 to 33	17.5	15.8	.57	26.2	4.45	28.0

Exchange between Mn^{++} and the Mn from MnO_4^- during Precipitation. Experiments 2.1, 2.2.—A 101.0-ml. solution which was 1.116 × 10^{-3} molar in $KMnO_4$ (6.19 mg. Mn) was poured rapidly into 105.0 ml. of a 2.57 × 10^{-3} molar $Mn^*(ClO_4)_2$ (14.8 mg. Mn) solution which was also 5.6 × 10^{-2} molar in $HClO_4$ at 25 ± 1°. The mixture was stirred immediately, then allowed to stand without further mixing. A fading of the permanganate color was detectable in 1 min., which was followed by a rapid precipitation. Precipitation appeared complete at 3 minutes from the absence of the pink color. The solution was transferred to centrifuge tubes, and 7 and 14 ml. of wash H_2O needed to assist the transfer were added to the mixtures of experiments 2.1 and 2.2, respectively. The solutions were centrifuged during the interval of 12 to 23 minutes after the mixing.

Experiment 2.3.—The mixing conditions were identical in this experiment to 2.1 and 2.2 except that the 105.0 ml. of $Mn^*(ClO_4)_2$ solution was 0.112 molar in $HClO_4$. Fading was discerned in 1 min., a visible precipitate appeared 2 min. later and the pink color had disappeared 10 min. after mixing. The mixture was transferred to centrifuge tubes with the aid of 4 ml. of wash H_2O. Centrifuging continued during the interval of 15 to 25 min. after the mixing.

The treatment of the centrifugate and precipitate followed the procedure in experiments 1.1–1.5. The analyses of the two fractions permitted a check of the recovery of manganese, and the specific activities of the manganese in both the precipitate and the solution phases were determined. Results have been collected in Table II.

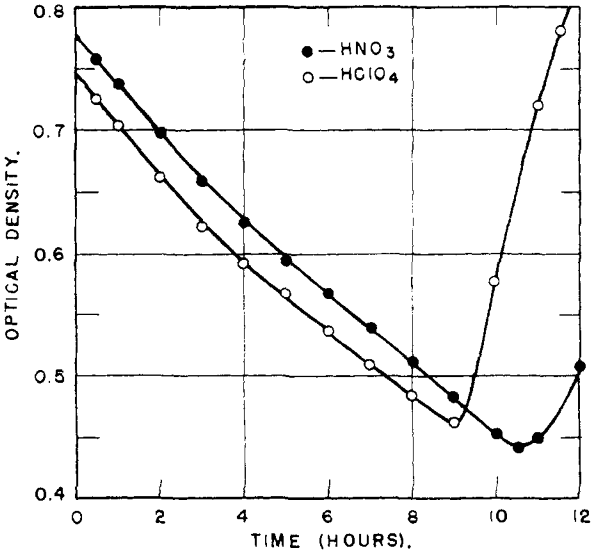

Fig. 1.—Absorption of light by a solution of $KMnO_4$ and $MnSO_4$ *versus* time; initial concentrations, $KMnO_4$ = 3.5 × 10^{-4} molar, $MnSO_4$ = 8.7 × 10^{-4} molar, acid = 2 molar.

TABLE II

EXCHANGE OF MANGANESE DURING THE PRECIPITATION REACTION BETWEEN Mn^{++} AND MnO_4^- AT 25°

Expt.	Time ppt. centri-fuged, min.	Mn found, mg. As Mn^{++}	As ppt.	(α − 1)	*Specific* activity, ct. /min. mg. Mn In Mn^{++}	As ppt.	$\frac{S_0^{II} - S^{II}}{S_0^{II} - S_\infty}$ f(%)
2.1	12–23	4.43	16.6	0.59	207	205	98 ± 0.9[a]
2.2	12–23	4.40	16.4	.59	214	206	93 ± 1.1
2.3	15–25	4.74	16.2	.61	205	202	98 ± 1.1

[a] Indicated errors are statistical standard deviations from the counting.

Exchange between Mn^{++} and MnO_4^-.—A solution of $Mn^*(ClO_4)_2$ and HNO_3 with a volume of 105.0 ml. was placed in a thermostated flask at a temperature of 25.0 ± 0.1°. A small volume of a 9.36 × 10^{-2} molar $KMnO_4$ was pipetted into the flask which was shaken to mix the contents. At subsequent times 13.0-ml. aliquots were withdrawn from the flask and added to 10 ml. of a 8.19 × 10^{-3} molar $(As(C_6H_5)_4)NO_3$ solution. The mixture was allowed to stand with occasional stirring for 3 min.; then the precipitate was collected on a filter paper in the chimney-type filter. The precipitate was washed 6 times with 5-ml. portions of 2.7 × 10^{-4} molar $(As(C_6H_5)_4)NO_3$ solution and once with 5 ml. of H_2O. It was dried in air, weighed for the determination of a self scattering correction, and mounted for counting. Later, the manganese contents were determined by analyses so the specific activities of the precipitates were obtained. The conditions and results of 3 experiments are included in Table III. The apparent fraction of exchange was calculated from the expression, $f = S/S_\infty$, for the precipitates. The very low exchange in the early samples indicated that the separation process did not induce exchange.

It was noted during these experiments that the exchange solutions seemed to fade even though a visible precipitate did not form. For a quantitative measure of this fading, the light absorption at 525 mμ (a peak of the permanganate spectrum) of 3.5 × 10^{-4} molar $KMnO_4$ solutions which were 2.00 molar in HNO_3 and $HClO_4$ was followed for several hours. A 16% reduction of the light absorption in the $HClO_4$ solution and a 10% reduction in the HNO_3 solution corresponded to first order half-lives of 32 and 53 hours, respectively. Results with similar solutions which contained, in addition, 8.7 × 10^{-4} molar $MnSO_4$ are shown in Fig. 1. A first order reduction in the light absorption with a half time of 12 hr. was obtained in each acid. The appearance of the precipitate is clearly evident in the figure.

Results and Discussion

Exchange between Mn^{++} and Freshly Formed Precipitates.—The precipitates were formed in a solution of low acidity so that the exchange measurements could be started quickly. An excess of Mn^{++} was present so that reaction of the Mn^{*++} with the precipitate which might result in the actual deposition of the radioactive Mn^{++} on the precipitate would be minimized. The amount of Mn^{*++} added was roughly equal to the excess Mn^{++}. Some possibility for deposition of the tracer on the precipitates did exist because of the high momentary local concentrations of Mn^{*++} during its addition to the solution. It can be calculated from the data in Table I that *ca.* 1.4 mg. of the Mn^{*++} entered the precipitate. If this was the result of a deposition process, then the precipitate must have been formed with an (α − 1) of 0.66 which is badly out of line with the values which were found in experiments 2.1, 2.2 and other precipitation experiments. The amount of Mn finally in the precipitate and in the solution were approximately equal, so the compositions of both phases were determined with equal accuracies.

It has been concluded from the data in Table I

TABLE III

ISOTOPIC EXCHANGE BETWEEN Mn^{++} AND MnO_4^- AT 25°

Initial concn., moles/l.			Exchange time, hr.	Wt. Mn in ppt., mg.	S^{VII}, ct./min. mg. Mn	S_∞	Apparent fraction exchange, %	$R_0 \times 10^6$ moles/l. hr.	$R_0 \times 10^6$, eq. 3 moles/l. hr.
Mn^{++} $\times 10^4$	MnO_4^- $\times 10^4$	HNO_3							
8.89	5.68	1.0	0.50	0.102	2.0 ± 2.5[a]	121.8	1.6	1.6	1.8
			1.00	.082	4.1 ± 2.8	121.3	3.4		
			2.00	.087	13.9 ± 2.5	121.0	11.5		
			2.50	.070	19.1 ± 3.2	120.5	15.9		
			4.00	.165	15.4 ± 2.2	119.4	12.9		
8.89	3.57	2.0	0.0	0.210	0 ± 1.2	124.5	0	2.0	3.9
			1.00	.130	11.8 ± 2.4	128.7	9.1		
			2.00	.115	29.6 ± 2.3	126.2	23.5		
			3.00	.130	24.2 ± 2.3	124.8	19.4		
			4.00	.124	34.9 ± 2.3	126.4	27.6		
			5.00	.110	39.6 ± 1.8	125.0	31.7		
			6.50	.102	46.9 ± 2.3	126.7	37.0		
13.5	2.68	1.0	0	0.155	1.0 ± 1.4	142.3	0.7	1.4	2.5
			0.50	.110	8.4 ± 1.9	141.8	5.9		
			1.00	.113	8.2 ± 2.4	143.0	5.8		
			2.00	.106	19.1 ± 2.8	141.4	13.5		
			3.00	.099	24.4 ± 2.6	143.3	17.1		
			3.50	.095	24.0 ± 2.5	141.0	17.0		
			4.00	.072	35.4 ± 3.6	145.5	24.3		

[a] Indicated errors represent standard deviations from counting statistics only.

that the precipitates underwent a real exchange of 28 to 39% in one to two minutes. However, additional exchange was so slow that it was scarcely detectable in an additional 20–30 min. A major fraction of the precipitates was excluded from such a rapid exchange within one to two min. of their formation.

In working with the slower exchange involving well-aged oxides, Jordan[10] proposed that low oxidation states of Mn in precipitates exchanged rapidly with Mn^{++} in solution, but that Mn^{IV} exchanged much more slowly. The analogous possibility must be considered in these experiments. In experiment 1.1, the average Mn oxidation state in the precipitate was calculated to be 3.82 from the amounts of MnO_4^- and Mn^{++} which had reacted. A minimum amount of Mn^{IV} would be present if 18% of the precipitated Mn were Mn^{III}. In such a case the ratio of the specific activities, $S^{\mathrm{IIIp}}/S^{\mathrm{IIL}}$, is 1.38; *i.e.*, a concentration of activity would have occurred in the precipitated Mn^{III}. (Superscripts II, III, IV and VII indicate the oxidation state of a fraction, and superscripts p and L indicate the precipitated and solution forms, respectively.) A concentration of activity in the precipitate might occur by a recrystallization process. Myers and Prestwood[11] have reviewed the evidence concerning the concentration of activities by recrystallization in heterogeneous exchange experiments. However, there is an upper limit to the extent of concentration which can be attained. A maximum concentration is produced by a single complete recrystallization of the precipitated fraction on a differential scale. It can be shown that the maximum specific activity ratio for recrystallization would be

$$S^{\mathrm{IIIp}}/S^{\mathrm{IIL}} = (e^r - 1)/r \qquad (9)$$

where $r = (Mn^{\mathrm{IIIp}})/(Mn^{\mathrm{IIL}})$, and the parentheses signify the weight of manganese in mg. This expression is in agreement with the limit of the expression given by Kolthoff and Rosenblum[12] when their fraction of recrystallization, (a/d), is set equal to $1/n$, where n is the number of recrystallizations, and n is allowed to increase indefinitely. Expression 9 allows a maximum of 1.10 for the ratio, $S^{\mathrm{IIIp}}/S^{\mathrm{IIL}}$, and the experimental result is not consistent with such a mechanism. For all the other experiments of Table I the ratio of $S^{\mathrm{IIIp}}/S^{\mathrm{IIL}} \leq 1$. The extent of exchange for all the experiments was too great to have resulted from exchange between Mn^{++} (aq) and the Mn^{II} in a precipitate containing only Mn^{II} and Mn^{IV}.

An alternative postulate might allow all the Mn in the precipitate on or near a surface to exchange with Mn^{++} in solution. However, the Mn in the interior of large particles is removed from contact with the solution and excluded from a rapid exchange. Recrystallization can still play a role in the process, especially if the exchange between Mn^{++} and the Mn^{IV} solution species occurs. However, the precipitate particles had grown or aged sufficiently in one to two minutes that a considerable fraction of the Mn had already been removed from exchange. Further aging had then to be slow as indicated by the results in the experiments 1.1, 1.2, 1.5.

The present results differ in some detail from those of Pullman and Haissinsky[9] which may reflect differences in conditions. However, their observation is confirmed that extensive but incomplete exchange takes place very rapidly for these precipitates. Polissar[6] may not have observed a significant exchange in his experiments because he used nearly stoichiometric amounts of Mn^{*++} and MnO_4^- to form a tagged precipitate containing $Mn^{*\mathrm{IV}}$. When he added inert Mn^{++} in large ex-

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[10] P. Jordan, *Helv. Chim. Acta*, **34**, 699 (1951).

[11] O. E. Myers and R. J. Prestwood, "Radioactivity Applied to Chemistry," A. C. Wahl and N. A. Bonner, Editors, John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 34–43.

[12] I. M. Kolthoff and C. Rosenblum, THIS JOURNAL, **58**, 116 (1936).

cess to the solution, the particle surfaces may have reacted rapidly with Mn^{++} to deposit an additional layer of hydrous oxide which covered the surface and prevented access of the tracer to the solution. Libby and Adamson[8] concluded that exchange with colloidal sols was slow; however, their one experiment with low precision was not inconsistent with an only partial but rapid exchange.

Exchange between Mn^{++} and Mn from MnO_4^- during Precipitation.—The precipitation was effected in the presence of excess Mn^{*++}. Again, the activity and Mn content of both the solution and precipitate fractions were determined so the extent of exchange could be calculated from the specific activity of either fraction. Within reasonable limits for experimental accuracy the tracer was distributed uniformly between the two phases. Consider the Guyard reaction to be represented schematically by the expression

$$\begin{tikzcd}
 & & \alpha \mathrm{Mn}_{\mathrm{ppt-aged}} \\
(\alpha - 1)\mathrm{MnO_4}^- + \mathrm{Mn}^{++} \arrow[r] \arrow[rr, dash, bend right, "30\text{–}40\% \text{ exchange}"'] & (\text{Intermediates}) \arrow[r] & \alpha \mathrm{Mn}_{\mathrm{ppt}} \arrow[u]
\end{tikzcd} \qquad (10)$$

If there were no exchange between Mn^{++} and Mn^{IV} in either the solution or the precipitate, the specific activity of the Mn^{++} should not have been reduced. It is apparent, however, that in either the homogeneous solution or in the initially formed precipitates, a complete exchange had occurred. If during the growth of precipitates the intermediates of reaction 10 never amounted to an appreciable fraction of the total Mn and if the intermediates exchanged completely with Mn^{++}, a concentration of activity in the precipitate should have occurred. If (Mn^*) equals the number of active atoms of Mn^{54} and (Mn) represents a weight of Mn(mg.), then for negligible amounts of intermediates,

$$-\alpha d(\mathrm{Mn}^{\mathrm{IIL}}) = d(\mathrm{Mn}^{\mathrm{p}}) \qquad (11)$$

For the complete exchange between the intermediates and Mn^{++}

$$-d(\mathrm{Mn}^{*\mathrm{IIL}}) = S^{\mathrm{IIL}} d(\mathrm{Mn}^{\mathrm{p}}) = -S^{\mathrm{IIL}} \alpha d(\mathrm{Mn}^{\mathrm{IIL}}) \qquad (12)$$

Therefore

$$d \log (\mathrm{Mn}^{*\mathrm{IIL}}) = \alpha d \log (\mathrm{Mn}^{\mathrm{IIL}}) \qquad (13)$$

If α is constant, integration of equation 13 gives

$$\log(\mathrm{Mn}^{*\mathrm{IIL}})/(\mathrm{Mn}^{*\mathrm{IIL}})_0 = \alpha \log (\mathrm{Mn}^{\mathrm{IIL}})/(\mathrm{Mn}^{\mathrm{IIL}})_0 \qquad (14)$$

and

$$\mathrm{S}^{\mathrm{IIL}}/S_0^{\mathrm{IIL}} = [(\mathrm{Mn}^{\mathrm{IIL}})/(\mathrm{Mn}^{\mathrm{IIL}})_0]^{\alpha - 1} \qquad (15)$$

From this expression it follows that for a completed precipitation yielding aged surfaces

$$S^{\mathrm{IIL}}/S_\infty = [1 + (\mathrm{Mn}^{\mathrm{VIIL}})_0/(\mathrm{Mn}^{\mathrm{IIL}})_0] \\ [1 - (\mathrm{Mn}^{\mathrm{VIIL}})_0/(\alpha - 1)(\mathrm{Mn}^{\mathrm{IIL}})_0]^{\alpha - 1} \qquad (16)$$

For the possible values, $5/3 > \alpha > 1$, the ratio, S^{IIL}/S_∞, is therefore less than 1.

In experiment 2.1 for which $(\alpha - 1)$ was 0.59, a value of 143 cts./min. mg. Mn is predicted for S^{IIL} by equation 15. The per cent. exchange, predicted from the formula, $100(S_0^{IIL} - S^{IIL})/(S_0^{IIL} - S_\infty)$, is 170%. Even with a 30% exchange between the precipitate and Mn^{++}, final values of $S^{IIL} = 161$ and $S^P = 217$ ct./min. mg. Mn are expected. Such a concentration of activity in the precipitate would have been very clearly indicated. From this result, it has been concluded that the intermediates of reaction 10 cannot be infinitesimal in magnitude, but a major fraction of the permanganate must have been reduced to Mn^{IV} which underwent exchange with Mn^{++} before an appreciable growth of particles or aging of the precipitates had occurred. The method of particle growth could not have been a reduction of MnO_4^- *in situ* to give an effective surface covering although the surface may have functioned as a catalyst for the reduction.

An initial precipitate might have formed without exchange of the Mn from the MnO_4^-. A complete differential recrystallization of this precipitate with exchange in the recrystallization process would also give a significant concentration of the activity in the precipitate. Some differences would be expected between the experiments 2.1 and 2.3 in which perceptibly different precipitation rates resulted from the change in acid concentration. Therefore, recrystallization does not appear to be a dominant factor in the exchange. Rather, it appears likely that the precipitates age or grow from a system which is already close to isotopic equilibrium. It cannot be concluded unambiguously that the rapid exchange between Mn^{++} and Mn^{IV} occurs in homogeneous perchloric acid solutions, for the surfaces of the freshly formed precipitates may play a role in the process. The exchange can reasonably occur by way of the disproportionation equilibrium

$$\mathrm{Mn}^{++} + \mathrm{Mn}^{\mathrm{IV}} \rightleftarrows 2\mathrm{Mn}^{\mathrm{III}} \qquad (17)$$

or by an oxygen atom transfer between the hydration-hydrolysis spheres of Mn^{++} and Mn^{IV}.

Homogeneous Reaction and Exchange between Mn^{++} and MnO_4^-.—It appears from Fig. 1 that in strongly acid solution a significant reduction of MnO_4^- occurs before the formation of a precipitate by a process which is not autocatalytic but which begins with a maximum rate. The reaction with Mn^{++} is considerably faster than the measurable spontaneous decomposition of MnO_4^-. It cannot be assumed therefore that a steady state with respect to Mn^{IV} is established. In 9 hours at least 40% of the MnO_4^- had been reduced, presumably to Mn^{IV}.

It is possible to exclude a mechanism for the disappearance of MnO_4^- from these solutions in which equilibria 4 and 17 are established in the solution with a rate-determining step.

$$\mathrm{MnO_4}^- + \mathrm{Mn}^{++} \longrightarrow 2\mathrm{Mn}^{\mathrm{IV}} \qquad (18)$$

This sort of mechanism accounts for the kinetics of the periodate oxidation of Mn^{++} and provides for increased over-all reduction rate of MnO_4^- as effective complexing agents for Mn^{+++} are introduced into the solution. If this mechanism were carrying the reaction under the conditions of the present experiments, the initial rate of disappearance would be significantly greater than the values given by the observed first-order function. It is felt that additional work is needed for the clarification of this reaction. These exploratory experiments have shown that the exchange mixtures containing Mn^{++} and MnO_4^- do not correspond to the classical case of homogeneous isotopic exchange in which no gross chemical change occurs. The ordinary treatment of the exchange must be modified. If in addition to process 5 there is a reaction of the type

$$Mn^{++} + MnO_4^- \longrightarrow \text{Products} \qquad (19)$$

the familiar first-order exchange law encountered in steady-state systems does not apply and the straight line relation

$$\log(1 - f) = kt \qquad (20)$$

cannot be expected. However, it can be shown that R_0, the exchange rate for reaction 4 under the initial conditions of the experiment, is given by

$$R_0 = [d \ln(1 - f)/dt]_0(Mn^{++})_0(MnO_4^-)_0/[(Mn^{++})_0 + (MnO_4^-)_0] \qquad (21)$$

In this equation the parentheses designate concentrations.

The apparent exchange fraction amounted to nearly 40% in one of the experiments in Table III. Since the data were not sufficient for the detection of curvature in the $\ln(1 - f)$ function, a least-squares straight line through the origin, $[\ln(1 - f) = 0, t = 0]$, was used to give the slope of the $\ln(1 - f)$ curve at $t = 0$. Values of R_0 obtained by this method are included in Table III together with the predictions of Adamson's formula (6). It is seen that the observed rates were lower in each case than the prediction of formula (6); however, the agreement was to within a factor of two in each case.

It is felt that there are serious objections to the consideration of the indicated values of R_0 as the actual rate of exchange between Mn^{++} and MnO_4^- for the solutions in which gross amounts of intermediate oxidation states have formed. The same apparent exchange would appear if the tetraphenylarsonium ion precipitated, together with the permanganate, some intermediate oxidation state which had exchanged with Mn^{++}. Likewise, in Adamson's experiments, if the precipitation upon the addition of hydroxide did not completely remove intermediate species, a similar apparent exchange would be indicated. In view of these possibilities the agreement of these results with those of Adamson does seem surprisingly good. However, it is believed that the exchange Mn^{++} and MnO_4^- cannot be considered as established.

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The Lower Oxidation States of Gallium. I. The GaI_3–GaI_2–GaI System*

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Gallium(II) iodide has been observed to disproportionate into gallium(III) iodide and gallium(I) iodide, instead of the trihalide and the metal that are obtained with gallium(II) chloride. A phase diagram and powder patterns confirm the existence of the two lower iodides. Gallium(II) iodide is only moderately stable at the melting point of 211°; gallium(I) iodide is sufficiently unstable that in the presence of excess gallium only a limiting composition of $GaI_{1.19}$ is obtained at a melting temperature of 265°. Gallium(I) iodide can be isolated from the limiting mixture by a solvent extraction. The demonstration of the existence of the gallium(I) oxidation state in this system may favor the formulation $Ga(I)[Ga(III)I_4]$ for the diamagnetic gallium(II) iodide.

Introduction

The first preparations of gallium(II) chloride, bromide and iodide were reported by Boisbaudran,[1] the discoverer of the element gallium, as resulting from the incomplete halogenation of the metal. Since that time, only the dichloride has received any significant attention, and Einecke[2] has even expressed doubt as to whether the diiodide was ever isolated. Klemm and Tilk[3] found solid $GaCl_2$ to be diamagnetic; accordingly the compound has usually been formulated as either $Ga(I)[Ga(III)Cl_4]$ or Cl_2Ga–$GaCl_2$.

The unsymmetrical structure has been somewhat unsatisfactory in that no Ga(I) halides have been isolated, although Ga_2S has been confirmed as a definite compound,[4] and Ga^+ appears to be formed by the anodic oxidation of the metal in glacial acetic acid.[5] The slight solubility of metallic gallium in liquid $GaCl_2$ first reported by Foster[6] might indicate the formation of a slightly stable GaCl. Measurements have shown that the clear solution contains about two mole per cent. gallium just above the melting point[7,8]; the metal is reprecipitated on solidification of the salt. Estimates of the stabilities of the gallium halides led Brewer[9] to predict that the monohalides would exist only in the gaseous state at higher temperatures.

(*) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

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