Retrospective Theses and Dissertations

1952

Manganese (II), (III), (IV) equilibrium in iodic acid

Glenn Raymond Waterbury

Iowa State College

NOTE TO USERS

MANGANESE(II), (III), (IV) EQUILIBRIUM

IN IODIC ACID

by

Glenn R. Waterbury

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State College

1952

UMI Number: DP13038

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI®

TABLE OF CONTENTS

I. INTRODUCTION

The complex nature of the mechanisms involved in the reaction of manganese(II)[1] with permanganate, the reduction of permanganate by oxalate, and the oxidation of manganese(II) to permanganate by any of a number of suitable oxidizing agents has stimulated the interest of numerous investigators since the early studies of Gorgeau (1), Guyard (2), Harcourt and Esson (3), and others. Several of the investigators have included the disproportionation reaction

$$2 \text{ Mn}^{III} \rightleftharpoons \text{Mn}^{IV} + \text{Mn}^{II} \qquad (1)$$
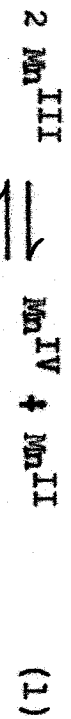
as an important step in the overall mechanism under investigation. In some cases the importance of a rapid manganese(II), (III), (IV) equilibrium has been emphasized by the assumption that either manganese(III) or manganese(IV) was the active oxidizing species. On the other hand some investigators have omitted this reaction entirely from their proposed mechanisms, or have indicated that if such an equilibrium existed, it was slowly established. Several attempts

---

[1] The Stock system of nomenclature has been used to avoid the confusion in the names of ions corresponding to the various oxidation states of manganese. The use of the term permanganate instead of manganese(VII) has been retained because of long established usage. The use of this system is in accord with the Report of the Committee for the Reform of Inorganic Nomenclature of the International Union of Chemistry, 1940.

(4, 5, 6, 7, 8, 9, 10, 11, 12) have been made to substanti-
ate the existence of a rapid manganese(II), (III), (IV)
equilibrium in the presence of fluoride ion, sulfuric acid,
oxalic acid, or phosphoric acid, and in some cases the magni-
tude of the equilibrium constant has been considered. How-
ever no study has been reported of the reaction in a system
containing iodate ion although a proposed mechanism for the
well known periodate oxidation of manganese(II) to perman-
ganate involves the manganese(II), (III), (IV) species in the
presence of iodate ion. The determination of the equilibrium
constant in a system which includes iodate and the study of
the factors influencing the equilibrium reaction are the sub-
ject of this work.

A. Previous Evidence for the Manganese(II),
(III), (IV) Equilibrium

Perhaps the most comprehensive and the best work on the
oxidation of manganese(II) to manganese(IV) by permanganate
was reported by Tompkins (4), who proposed that an intermedi-
ate product of the permanganate ion was manganese(III) which
disproportionated to manganese(II) and manganese(IV). The
subsequent hydrolysis of the latter to form manganese dioxide
was found to be retarded by agents which complexed and sta-
bilized the tervalent manganese ion. From his observations
he concluded that a rapid manganese(II), (III), (IV) equilib-

rium was established and that the presence of complexing
agents decreased the concentration of the quadrivalent ion.

Bassett and Sanderson (13) noted that a cherry-red color
was produced when permanganate was added to solutions of man-
ganese(II) sulfate strongly acidified with sulfuric acid. It
was their conclusion that the tervalent manganese formed in
the reaction

$$MnO_4^- + 4\ Mn^{II} + 8\ H^+ \longrightarrow 5\ Mn^{III} + 4\ H_2O \quad (2)$$
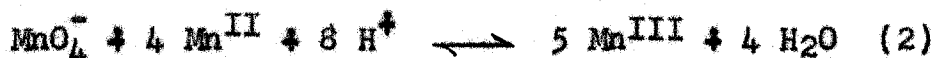
was converted into relatively stable sulfate complexes of
manganese. Since the color of the solutions persisted for
several days in the absence of oxidizable material, and then
precipitated manganese dioxide with an accompanying reduction
in color intensity, they postulated a slow manganese(II),
(III), (IV) equilibrium. Corresponding reactions in phos-
phoric and oxalic acid solutions led to similar conclusions
concerning the equilibrium in these systems.

Polissar (6) added support to the postulated equilibrium
in oxalic acid solution and suggested that systems in which
fluoride ion was the complexing agent behaved in a like man-
ner. He reported that the amount of oxalic acid oxidized by
a mixture of manganese dioxide and manganese(II) depended on
the ratio of manganese(II) to oxalic acid. In order to ex-
plain this dependence, the author postulated that the oxalic
acid could either be oxidized or could form a stable manga-
nese(III) oxalate complex. The presence of manganese(II)

would permit the formation of manganese(III), due to the equilibrium reaction with the manganese(IV), and the tervalent manganese would then form an oxalate complex. Taube (14) reported that the manganese(III) oxalate complexes were not stable, and the rates of decomposition of the three species, $Mn(C_2O_4)_3^{---}$, $Mn(C_2O_4)_2^{-}$, and $MnC_2O_4^{+}$ were given. Since these rates were slower than the rate of oxidation of oxalic acid by manganese dioxide, Polissar was able to make rapid measurements before significant amounts of the complexes had decomposed.

In addition to the above work, Polissar (7) used radioactive manganese as a tracer in a search for possible equilibrium reactions in solutions containing manganese in two valence states. He found that a rapid and complete exchange occurred between manganese(III) oxalate and manganese(II) ion. These results were interpreted by the author to indicate the existence of an equilibrium between manganese(III) oxalate ion, manganese(II) ion, and manganese(IV) in oxalate solution.

The most recent study of the manganese(II)-permanganate system was that of Adamson (15). From his investigation of the exchange reaction between manganese(II) and permanganate ions in acid solution, he postulated a slow forward reaction between the di- and the quadrivalent species but a rapid disproportionation of tervalent manganese in the presence of

solid manganese dioxide. The exchange studies were conducted

using solutions approximately 3 M in perchloric acid. No

agent was added to stabilize the manganese(III) species, and

in most cases solid manganese dioxide was formed. These com-

plicating factors led Adamson to include the following com-

ments in his article:

> 1. It does not seem possible to predict the course
> of reaction 3 once solid manganese dioxide has
> formed, since from this point the

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

> process is undoubtedly heterogeneous and not suscepti-
> ble to easy interpretation. Thus this mechanism will
> not serve to confirm or deny Tompkin's interpretation
> of his kinetic analysis of reaction 3. (15, p. 302)
>
> 2. In summary of the present state of knowledge of
> the manganese(II) permanganate reactions, it is fair
> to say that while some form of manganese(III) or man-
> ganese(IV) may be an active intermediate, the evidence
> to date bearing on the mechanism of their formation
> is unclear and the conclusions of previous investiga-
> tors are contradictory. (15, p. 294)

Recently an excellent survey of the studies of the re-

action between permanganate and oxalate ions was published by

Noyes (16), and this reaction need not be discussed in detail

here. However it is pertinent to point out a few of the pro-

posed mechanisms in which a manganese(II), (III), (IV) equi-

librium was postulated. Noyes did not include the equilib-

rium in his mechanism, but he did consider tervalent manga-

nese an important species in the overall reaction.

Launer and Yost (9) were among the first to consider the

disproportionation reaction in the permanganate-oxalate sys-

tem. In their studies they found that a large excess of fluoride ion prevented the formation of manganese(III) due to removal of manganese(II) as the fluoride. Lower fluoride concentrations increased the manganese(II) content, and the equilibrium was shifted almost completely in the direction of manganese(III) fluoride complex formation.

Bradley and Van Praagh (17) proposed from their study of the reaction between solid manganese dioxide and oxalic acid that manganese(IV) ions could be reduced to manganese(III) ions by the divalent species and that the reaction proceeded rapidly if some complexing agent was present to remove the tervalent ions as they formed. They cited as evidence for the rapid reversibility of reaction 1 the fact that manganese dioxide was rapidly dissolved by oxalic acid solution with a halving of the oxidizing titer, whereas if excess manganese (II) was present initially, the dissolution occurred with no loss in titer except for the subsequent gradual oxidation of the oxalic acid. Essentially, the dissolving of manganese dioxide by manganese(II) salts in oxalate and fluoride solutions was explained by a stabilization of the tervalent state due to formation of a complex. Adamson (15) preferred to explain the data obtained by Bradley and Van Praagh in terms of a reaction path involving species partially combined in a complex, e.g.,

$$Mn(C_2O_4)_2 \rightleftharpoons Mn^{++} + 2 Mn(C_2O_4)^+ , \qquad (4)$$
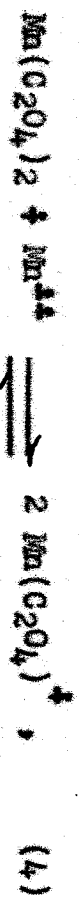
which did not require a rapid exchange in the absence of a complex forming agent.

McBride (18) did not propose a manganese(II), (III), (IV) equilibrium as such but indicated the existence of two possible reactions between permanganate and manganese(II) as follows:

$$MnO_4^- + Mn^{II} \rightleftharpoons \begin{matrix} Mn^{III} \\ \text{or} \\ Mn^{II} + Mn^{IV} \end{matrix} \qquad (5)$$
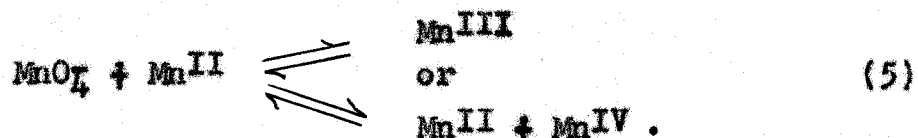
Abel (19) and others (8, 20, 21, 22) indicated the existence of the equilibrium, but they made no intensive study of the subject.

Heintze and Mann (23) found that a rapid equilibrium existed between the di-, ter-, and quadrivalent manganese states in pyrophosphate solution. It was their belief that the reversible reaction,

$$MnO + MnO_2 \rightleftharpoons Mn_2O_3 , \qquad (6)$$

was of a general nature applicable to some of the other transition elements. Watters and Kolthoff (10) reported the structure of the tripyrophosphate complex of manganese(III) to be a chelate type anion having the formula $Mn(H_2P_2O_7)_3^{3-}$. At a pH of 7 the color of the complex changed from violet to amber, and as the pH was increased, a precipitate formed due to the disproportionation of the complex to manganese dioxide and manganese(II) ion. The $Mn^{II} - Mn^{III}$ complex system showed a reversible potential at a platinum electrode; the

potential for equimolar Mn^{II} - Mn^{III} in 0.4 molar sodium
pyrophosphate at a pH of 2.06 was 1.013 $\pm$ 0.003 volts when
referred to the hydrogen electrode.

Of the various methods available for the oxidation of
manganese(II) to permanganate, the use of periodic acid and
the mechanism involved has been discussed most completely in
recent literature. Strickland and Spicer (24), in their de-
tailed discussion of the periodate oxidation, included the
following form of equation 1 in their proposed mechanism:

$$Mn^{++} + MnO^{++} + 2 H^+ \rightleftharpoons 2 Mn^{+++} + H_2O . \quad (7)$$
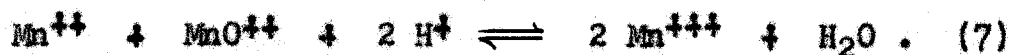
However they stated that the reaction proceeded only in the
presence of a complexing agent that kept the manganese(III)
ion concentration small and prevented the formation of man-
ganese dioxide. Waterbury, Hayes, and Martin (25) also pro-
posed the rapid establishment of the manganese(II), (III),
(IV) equilibrium in the periodic acid oxidation, but a com-
plete investigation of the reaction was not given at that
time.

B. Previous Measurements of the Equilibrium Constants

The preceding discussion has shown that an equilibrium
probably is established between the manganese(II), (III), (IV)
species in solutions that contain agents which are known to
complex the tervalent state. Neither the rapidity of the
establishment of the equilibrium nor the magnitude of the
equilibrium constant has been considered in any but a quali-

tative manner in the references cited. The only work reported which has dealt with the quantitative determination of the equilibrium constant is that of Grube and Huberich (12) for a system 7.5 molar in sulfuric acid and by Grube and Staesche (26) for manganese in concentrated phosphoric acid solutions. These authors considered the reaction was rapid but gave no supporting evidence for this assumption. In both cases the equilibrium constants were calculated from the differences in the potentials measured with solutions containing equal concentrations of manganese(II) and manganese(III) and solutions containing equal concentrations of manganese(III) and manganese(IV). The following set of equations were developed to show the feasibility of this procedure.

For the reactions, $Mn^{II} \longrightarrow Mn^{III} + e^-$

and $Mn^{III} \longrightarrow Mn^{IV} + e^-$,
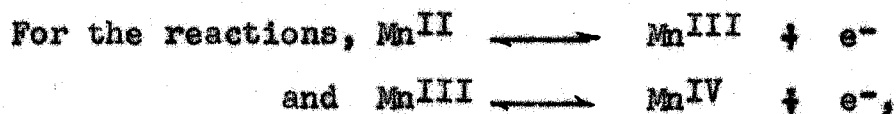
the Nernst equations were used in the following form:

$$E_1 = E_1^0 - \frac{RT}{nF} \ln C_3/C_2 \qquad (8)$$

$$E_2 = E_2^0 - \frac{RT}{nF} \ln C_4/C_3 \qquad (9)$$

where C_2 was the concentration of Mn^{II}, C_3 was the concentration of Mn^{III}, and C_4 was the concentration of Mn^{IV}. At equilibrium these potentials were equal, and the following equation was obtained:

$$(E_2^0 - E_1^0)F/RT = \ln C_2 C_4/C_3^2 = \ln K_c . \qquad (10)$$

The cell used in measuring the potentials consisted of a

normal calomel reference electrode and the half cell Pt;
Mn^{III}, Mn^{II} or Pt; Mn^{IV}, Mn^{III} which may be represented as
follows:

Hg; Hg_2Cl_2, KCl(1N):: H_2SO_4 (7.5M), Mn^{III}, Mn^{IV}; Pt and

Hg; Hg_2Cl_2, KCl(1N):: H_2SO_4 (7.5M), Mn^{II}, Mn^{III}; Pt.

The manganese solutions, which were prepared by electrolytic
oxidation of a manganese(II) sulfate solution in strong sul-
furic acid, were analyzed gravimetrically for total manganese
content, and the relative amounts of the various oxidation
states present were determined by titrating the solutions
with standard ferrous ammonium sulfate. Solutions of equal
manganese(II) and manganese(III) concentrations and solutions
of equal manganese(III) and manganese(IV) concentrations were
prepared from the analyzed solutions described above, and
potential measurements were made on these solutions at 12°C.
Since the equilibrium constant for the disproportionation of
manganese(III) was quite small in concentrated sulfuric acid
solutions, the calculation of the Mn^{II}/Mn^{III} and Mn^{III}/Mn^{IV}
ratios was simplified.

At 12°C in 7.5 molar sulfuric acid the observed values
for $E_{Mn^{II}/Mn^{III}}$ and $E_{Mn^{III}/Mn^{IV}}$ were 1.511 volts and 1.642
volts respectively, referred to the hydrogen electrode. Us-
ing these values, the equilibrium constant as given in equa-
tion 10 was calculated to be 5.032×10^{-3}. The authors then
obtained a "corrected equilibrium constant", K_0, from the

observed constant using the following argument. In the manganese(II)-manganese(III) solutions, the ratio of the concentrations of the two species was not one due to the equilibrium reaction. If 2x parts of manganese(III) disproportionated according to the reaction,

$$2 \; Mn^{III} \; \rightleftharpoons \; Mn^{II} + Mn^{IV} \tag{11}$$

$$2x \qquad\qquad x \qquad x$$
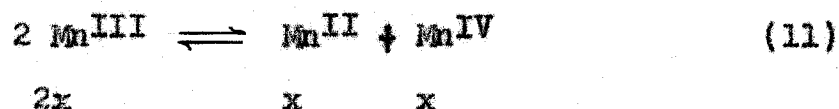
the ratio became:

$$\frac{C_3}{C_2} = \frac{1 - 2x}{1 + x} \quad \text{and} \quad \frac{C_4}{C_2} = \frac{x}{1 + x} . \tag{12}$$

When these corrections were made, the following relationship was obtained between K_o and K_c:

$$K_o = K_c/(1 - 3K_c)^2 . \tag{13}$$

Using the above equations, the corrected equilibrium constant for the disproportionation reaction in 7.5 M sulfuric acid at 12°C became 5.187×10^{-3}, a correction of approximately four per cent. As the constant decreased, the correction became smaller and less important.

The authors reported a marked inverse dependence of the equilibrium constant on the sulfuric acid concentration. Using 12.1 M sulfuric acid, K_o was calculated to be 1.3×10^{-3} at 12°C; using 4.6 M sulfuric acid, K_o was 6.98×10^{-2}.

Using similar procedures and calculations, Grube and Staesche (26) determined the equilibrium constant in concentrated phosphoric acid. The potentials of solutions contain-

ing 0.005 gram atoms of manganese per liter and various phosphoric acid concentrations were measured at 17°C. K_0 values varied from 8.0×10^{-5} at 10.0 N phosphoric acid to 1.4×10^{-1} at 40 N H_3PO_4.

Vetter and Manecke (11), in their recent paper on the primary mechanisms involved in the electrochemical potentials of the Mn^{II} ion/Mn^{III} ion system and the Mn^{III}/Mn^{IV} ion system, discussed the earlier work of Grube and his co-workers. It was their belief that the constant was reported with an accuracy greater than experimental difficulties would permit. The use of a calomel electrode in a sulfate solution created a liquid junction potential which could not be estimated accurately. However probably greater error was introduced in the preparation of the standard manganese solutions. Vetter and Manecke were troubled by oxygen evolution in the strong sulfuric acid solutions and the reduction of part of the manganese(III) and manganese(IV) ions; even careful preparation techniques carried out at 5°C failed to eliminate this difficulty especially in the quadrivalent manganese solutions. Due to this definite uncertainty in the potential measurements and to the unknown size of the error caused by the oxygen evolution and manganese(IV) reduction, they concluded that the exactness of the equilibrium constant was not great. At 25.0°C in 7.5 M sulfuric acid, a K of 1.7×10^{-3} was indicated by their data, but they preferred to state only that

the equilibrium constant was less than 7×10^{-3}.

In addition to their work on the equilibrium constant, Vetter and Manecke developed mechanisms for the electrode reactions in the manganese system under current flow. Since the method employed to determine the equilibrium constant in the present work was based on potential measurement of the manganese system, their results were pertinent. They constructed a number of current-potential plots using various concentrations of manganese. The slopes of the curves obtained were dependent on the manganese(III) concentration but independent of the manganese(IV) and manganese(II) concentrations. This indicated that the potential determining reaction was:

$$Mn^{+++} + e^- \rightleftharpoons Mn^{++} . \tag{14}$$

The apparent reaction

$$Mn^{++++} + e^- \rightleftharpoons Mn^{+++}. \tag{15}$$

as stated by Geloso (27), did not exist as a one step mechanism but consisted essentially of the following two steps:

$$Mn^{+++} + e^- \rightleftharpoons Mn^{++} \tag{16}$$

$$Mn^{++} + Mn^{++++} \rightleftharpoons 2\,Mn^{+++} \tag{17}$$

$$Mn^{++++} + e^- \rightleftharpoons Mn^{+++} . \tag{18}$$
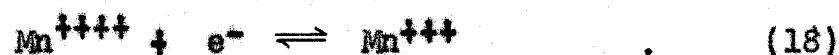
Confirmation was thus given here for the existence of the manganese(II), (III), (IV) equilibrium, and an insight into the overall reaction was obtained.

In summarizing the work reported to date it may be said

that the evidence points strongly to the existence of an

equilibrium reaction between the di-, ter-, and quadrivalent

manganese species in solution and that the presence of an

agent which complexes manganese(III) and manganese(IV) formed

in the reaction permits a study of the reaction in a homogene-

ous system. Most of the investigators have assumed or deter-

mined that the equilibrium was attained rapidly; there was

some controversy on this point however. The magnitude of the

equilibrium constant and the factors influencing the reaction

have been determined for sulfate and phosphate systems al-

though a question has been raised by recent authors concern-

ing the accuracy of the determinations. In the present work

the equilibrium was studied in an iodate system to determine

the rapidity of the attainment of equilibrium, the magnitude

of the equilibrium constant under various conditions, and

some of the factors influencing the reaction.

II. EXPERIMENTAL

A. Materials

Ammonium Hydroxide, NH_4OH: Baker and Adamson reagent grade. Sp. Gr. 0.90; 28% NH_3.

Iodic acid, HIO_3: G. Frederick Smith Chemical Company, Columbus, Ohio. GFS reagent of purity better than 99.9%. Solution: Iodic acid crystals dissolved in water and allowed to stand overnight. The solution was filtered through a fine sintered glass filter.

Lithium carbonate, $LiCO_3$: Baker and Adamson reagent grade.

Lithium perchlorate, $LiClO_4 \cdot 3H_2O$: G. Frederick Smith Chemical Company, Columbus, Ohio. GFS reagent. Solution: Lithium perchlorate crystals dissolved in water and filtered.

Manganese metal, electrolytic of a purity of 99.99%.

Manganese dioxide, MnO_2: Baker and Adamson reagent grade.

Manganous Sulfate, $MnSO_4$: Baker and Adamson reagent grade.

Perchloric acid, $HClO_4$: Baker and Adamson reagent grade. 70-72% $HClO_4$.

Periodic acid, H_5IO_6: G. Frederick Smith Chemical Company, Columbus, Ohio. GFS reagent of purity better than 99.99%.

Potassium acid iodate, $KH(IO_3)_2$: G. Frederick Smith

Chemical Company, Columbus, Ohio. GFS reagent of purity bet-
ter than 99.99%. This salt was used as a primary standard
for iodate and for acid standardizations.

Potassium iodate, KI: Baker's analyzed chemical reagent.

Potassium permanganate, $KMnO_4$; Baker and Adamson reagent
grade.

Silver nitrate, $AgNO_3$; Baker's analyzed chemical reagent.

Sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$: Baker's analyzed chemi-
cal reagent.

Sulfuric acid, H_2SO_4; Baker and Adamson reagent grade.
Sp. Gr.: 1.84; 95-96% H_2SO_4.

These chemicals were of a quality to meet A. C. S.
Standards as were all other chemicals used.

B. Preparation of Solutions

The preparation of the manganese solutions was compli-
cated by interaction of the iodate with the various manganese
species. Considerable time and effort was required to pre-
pare a solution containing predominantly manganese(IV). On
the other hand, solutions of manganese(II), which could be
prepared fairly simply, were not stable for long periods of
time. These difficulties warrant a brief discussion of the
methods employed in preparing and using the manganese solu-
tions.

Manganese(II) solutions were generally prepared by add-

ing a slight excess of the sulfate salt to an iodic acid
solution to saturate it with manganese(II) iodate. The man-
ganese(II) iodate, which precipitated during a ten to fifteen
minute agitation period, was removed by filtration through a
fine sintered glass filter. This method introduced sulfate
ion in very low concentration into the solutions; however,
since the ratio of iodic acid to sulfuric acid was approxi-
mately 10^4, no effect due to the sulfate could be discerned.

A second method of preparation which did not introduce
sulfate ion was the dissolution of manganese metal in iodic
acid directly. The metal dissolved slowly in hot concen-
trated iodic acid solutions with an evolution of hydrogen
gas. However, under these conditions the iodate oxidized the
manganese rapidly yielding a pale violet solution which con-
tained manganese(III) and manganese(II). A corresponding re-
action occurred in dilute manganese(II) iodate solutions at
room temperature, but the oxidation was very slow. The
iodate decomposition was evidenced, after samples had stood
for several days, by the development of the characteristic
pink-violet color of manganese(III) and by formation of small
crystals of iodine on the glass walls of the container. Be-
cause of this decomposition reaction, the solutions were pre-
pared from manganese(II) sulfate instead of manganese metal
and were used within a few hours when spectrophotometric
analyses failed to detect manganese(III) or iodine absorption
peaks.

Two methods were tried also for the preparation of the brown quadrivalent manganese solutions. The most obvious and first tried procedure consisted of the dissolution of manganese dioxide in iodic acid. Commercial MnO_2 did not dissolve readily and warming of the solutions was required. Here again decomposition occurred, and a violet solution containing more manganese(III) than manganese(IV) was obtained. Since freshly precipitated hydrous manganese dioxide is more soluble, samples were prepared from permanganate and sodium thiosulfate or manganese(II) sulfate. The precipitate was washed carefully to remove foreign ions but not dried. Iodate solutions of this oxide were satisfactory only in rare cases; in general colorimetric analyses showed a manganese(III) concentration equal or greater than that of manganese(IV).

Several investigators (28, 29, 30, 31) have studied manganese dioxide and have reported that different varieties of the compound exist. In addition, it has been found that large amounts of tervalent manganese are present in most samples. In an attempt to prepare manganese dioxide which contained mostly quadrivalent manganese, the precipitation reactions discussed above were carried out using large excesses of permanganate. The results were no better. MnO_2 was prepared also by adding periodic acid to a concentrated manganese(II) sulfate solution. As the oxidation proceeded, a dark, red-brown precipitate formed which presumably was a

periodate of manganese(IV). Upon washing with water, the precipitate turned dark brown in color as hydrolysis occurred. Since this product was practically insoluble in iodic acid, the hydrous precipitate from permanganate was used in most cases. By preparing several solutions from different manganese dioxide samples, an occassional solution was obtained in which the tervalent manganese concentration was low compared to that of the quadrivalent species.

The second method of preparation of manganese(IV) solutions was the oxidation of manganese(II) or manganese(III), (IV) iodate solutions with calculated amounts of periodic acid. In order to avoid sulfate ion and to keep the amount of periodate added to a minimum, solutions prepared from hydrous MnO_2 were usually used. As discussed in a later section, manganese(IV) iodate solutions could not be obtained pure but always contained either the higher or lower oxidation states. Consequently, only sufficient periodate was added to partially oxidize the manganese(III) content; in this manner the presence of periodate and permanganate in the titrating solutions was avoided.

No interaction between manganese(IV) and iodate was evident in solutions stored in glass stoppered containers. However, unstoppered solutions were reduced over a period of several days as indicated by the change in color from brown or amber to violet. Due to the low manganese concentrations,

sufficient oxidizable impurities from the air could have been
absorbed to cause the reduction and no interaction with iodic
acid was indicated. A very small amount of red-brown pre-
cipitate did form slowly in the manganese(IV) solutions which
were stored in glass; no solid of this type precipitated when
the containers were fused quartz. This evidence indicated
that some constituent leached from the glass containers was
causing the precipitate to form. Several authors (32, 33,
34, 35, 36) have discussed ter- and quadrivalent manganese
complexes. Olsson (37) has described insoluble double iodates
of the type $M_2Mn^{III}(IO_3)_5$ where M is potassium, rubidium,
cesium, or ammonium ion. However, these compounds were yel-
low or yellowish brown in color. Double iodates of quadri-
valent manganese, as reported by Berg (38), were formed
easily with potassium or ammonium ion and were violet brown
in color. Prepared samples of the potassium salt, $K_2Mn(IO_3)_6$,
closely resembled the precipitate obtained in the manga-
nese(IV) solutions. Spectrographic analysis of the precipi-
tate performed by Duane Johnson of this laboratory indicated
a potassium content of 5 - 10%; the calculated value was
6.6%. It was concluded that the substance precipitating from
the manganese(IV) solutions was the double salt, potassium
manganese(IV) iodate.

The manganese(IV) solutions were cloudy when freshly
prepared, and some of the apparently clear solutions ex-

hibited the Tyndall effect. However, after filtration and dilution to concentrations suitable for use in the titrations, the cloudy or colloidal properties were no longer evident. To avoid errors due to decomposition, the solutions were used on the same day that they were prepared. If slight changes in color occurred or if a precipitate or cloudiness was evident, the solutions were discarded.

The preparation of the lithium iodate solution should be mentioned here also although the procedure was straightforward. A weighed amount of dry lithium carbonate was dissolved in an equivalent amount of standard iodic acid solution. When solution was complete, the pH was adjusted to 5 using lithium hydroxide and iodic acid, and the solution was filtered and analyzed.

C. Apparatus

Spectrophotometric measurements were made using a Cary Recording Spectrophotometer manufactured by the Applied Physics Co., Pasadena, California, or a Beckman DU Quartz Spectrophotometer manufactured by Beckman Instruments Co., South Pasadena, California. Both instruments have a quartz optical system enabling the operator to work in the ultraviolet and visible regions with light which could be considered essentially monochromatic. In the Cary instrument the light beam is split by the optical system, half passing

through the blank and the other half through the sample cell after which the light falls upon photocells. The signals from the photocells are amplified electronically in a differential amplifier, impressed across a logarithmically wound resistor, and measured by a Brown recording potentiometer. This makes possible the presentation of the light absorbing characteristics of the sample directly in absorbance units.[1] The accuracy which may be attained with this instrument ranges from 0.5% at absorbancies of less than one to about 0.2% at absorbancies between one and two. Since the Beckman instrument is not recording, all scanning of solutions was done using the Cary spectrophotometer. The Beckman was used in analytical procedures where readings at one or two wavelengths only were required. An accuracy of 0.1% is attainable with this instrument under ideal conditions. Caster (40) in a critical review of the possible errors in measurements with the Beckman spectrophotometer indicated an instrumental error of 0.5% for the determination of relative absorbancy values as in a series of unknowns when the read-

---

[1]The absorbance of a solution is defined as $A = \log_{10} I_0/I$ where A represents the absorbance, and I_0 and I the intensity of the light passing through the blank and the sample cell respectively. By using the combined Beer-Bauger law, this relation can be given also as

$$A = a_m c d$$

where c is concentration in moles per liter, d is the cell or sample thickness in centimeters, and a_m is the molar absorbancy index (39).

ings are about 0.400 to 0.500 units. Quartz cells with path lengths of 1.00 cm., 5.00 cm., and 10.00 cm. were used with both spectrophotometers.

A Beckman model G pH meter was used in the oxidation-reduction titrations and in the determination of hydrogen ion activity. This instrument was standardized with buffers prepared by the manufacturer for this purpose. Accuracies of 0.02 pH units or better than 2 millivolts are reported for this instrument. In the measurement of pH the glass electrode and standard calomel reference electrode supplied with the instrument were used. For the titrations of the manganese iodate solutions a platinum wire dipping into the solution served as the indicating electrode and a silver iodate half cell was used as a reference electrode. A discussion of the preparation and use of the silver iodate electrode is given in the appendix to this section.

D. Chemical Analyses

Periodate determinations were made as described by Willard and Diehl (41). The periodate was reacted with excess potassium iodide in acidified solution, and the liberated iodine was titrated with standard thiosulfate using starch as an indicator. Periodic acid was analyzed for both periodate and iodate using the method of Müller and Friedberger (42). The diluted sample was buffered with bicarbonate and treated with potassium iodide. At this acidity,

the periodate was reduced to iodate, and the liberated iodine was titrated with standard thiosulfate solution. A determination of total iodate and periodate yielded the concentration of each species.

Standard sodium thiosulfate solution was prepared in the manner described by Willard and Furman (43). After being stored for a week, the solution was standardized with potassium acid iodate as the primary standard using the same method employed for the determination of iodate.

The determination of iodate was made by adding excess potassium iodide to the acidified solution containing the sample. The liberated iodine was titrated with standard thiosulfate as in the periodate determinations.

Standard potassium permanganate solution was prepared by dissolving the reagent grade solid in water, boiling, and subsequent filtering through a sintered glass disk. Sodium oxalate was used as a primary standard for this material as in the method described by Fowler and Bright (44).

Lithium iodate and lithium perchlorate solutions were analyzed gravimetrically using a method given by Scatchard, Prentiss, and Jones (45). Aliquots of the solutions were evaporated to dryness and fumed with sulfuric acid. The residues were then ignited to constant weight at 900°C and weighed as the sulfates.

Standard acid and standard base solutions were prepared

by usual methods using potassium acid iodate as a primary standard.

E.   Colorimetric Analyses

The interaction of the various manganese species with iodic acid and the difficulties encountered in attempting to prepare pure solutions has been discussed previously. These difficulties presented a definite problem in the analysis of the manganese(IV) solutions required in the potentiometric titrations. No tested method was available for determining manganese(III) in the presence of manganese(IV). The small amounts of these species in the concentrated iodic acid solutions precluded consideration of any simple titrimetric procedure based upon oxidation or reduction of either the manganese(III) or manganese(IV) since iodic acid could be reduced easily itself. However, since the manganese in these oxidation states was colored, it became evident that perhaps the most feasible method for analyzing the solutions would be a colorimetric procedure.

As noted earlier, manganese(II) solutions in iodic acid remained colorless for several hours after preparation, and spectral scanning on the Cary spectrophotometer of freshly prepared solutions showed no absorption in the wavelength region from $400m\mu$ to $700m\mu$. It was assumed that these colorless solutions contained no manganese in any valence

state other than divalent, and the determination of total manganese content was sufficient to obtain the manganese(II) concentration. Total manganese was determined by periodate oxidation in acid solution to permanganate and colorimetric comparison with standard solutions as described by Willard and Greathouse (46) and others (47, 48). Since the permanganate color faded slowly in iodic acid solutions, the iodate was destroyed first by evaporation and fuming with sulfuric acid. This procedure was quite satisfactory for pure manganese(II) solutions but was not sufficient in itself for determining the concentrations of the higher oxidation states.

Hayes (49) has investigated the absorption character of the manganese(III) iodate complex in a qualitative manner but has given no absorbancy indices suitable for use in a colorimetric procedure. No information concerning the absorption characteristics of the manganese(IV) complex was found. Consequently the first step in developing a suitable analytical procedure for the complex solutions was the determination of absorbancy indices for the manganese(III) and manganese(IV) species. This presented a difficult problem due to the impossibility of preparing pure solutions of the ter- and quadrivalent states and to the overlap of the absorption peaks of manganese(III) and (IV) and permanganate.

The method employed to obtain the absorbancy indices consisted of scanning spectrophotometrically a standard solu-

tion of manganese(II) after each addition of a small amount of periodic acid. The solutions were heated after each addition to ensure complete reaction, and the volume and iodate concentration were kept constant by replacing to the cooled solutions any solvent which might have evaporated. By using sufficiently small increments of oxidant, a series of absorption curves were obtained which represented various mixtures of manganese(II), (III), and (IV) and permanganate; a few of the pertinent curves obtained from several series are reproduced in Figures 1 and 2.

In Figure 1, curve 1 represents a solution containing manganese(III) with a small concentration of manganese(IV). From curve 8, Figure 2, it was evident that manganese(III) does not absorb to any extent at 430 mμ ; consequently the absorbancy at that wave length in curve 1 was due to the quadrivalent state. Curves 2, 3, and 4 of Figure 1 showed increasing amounts of manganese(IV). Since the absorbancy increased at 430 mμ and 530 mμ, the absorbancy index for manganese(IV) at 530 mμ must be greater than that for the tervalent ion. A comparison of the absorption characteristics of manganese(III) and permanganate, as given in curves 8 and 9 of Figure 2, showed that both species absorbed strongly in the spectral region near 530 mμ and had low absorption near 430 mμ. The absorption peak at 530 mμ for manganese(III) was broad and smooth, but permanganate exhibited identifying fine

structure in this region. These differences served to distinguish between manganese(III) and permanganate in manganese(IV) solutions. Curve 5, Figure 1, represents a solution of quadrivalent manganese containing small amounts of manganese(III) or permanganate which caused the slight rise in the curve in the region of 530 mμ. Repeated attempts to obtain a solution in which no contribution to the spectra from manganese(III) or permanganate could be detected were unsuccessful; curve 5, Figure 1, shows the best available data. The rise in this curve at 530 mμ was too small to be useful in distinguishing the identity of the contaminant. As more periodic acid was added, the slight rise at 530 mμ became more pronounced, and irregularities which were clearly due to permanganate developed as shown in Figure 1, curve 6. It may be noticed also from these two curves that the absorbancy at 430 mμ increased with the addition of periodate and the resulting conversion of manganese(III) to manganese(IV). Curve 7, Figure 1, shows a mixture of permanganate and manganese(IV); the existence of the quadrivalent species was proved by the high minimum absorbancy at 430 mμ.

From a qualitative consideration of a series of curves of this type, it seemed possible to determine absorbancy indices for manganese(III) and manganese(IV) by measuring absorbancies at 430 mμ and 526 mμ for solutions of known total manganese content. At best a procedure of this type would
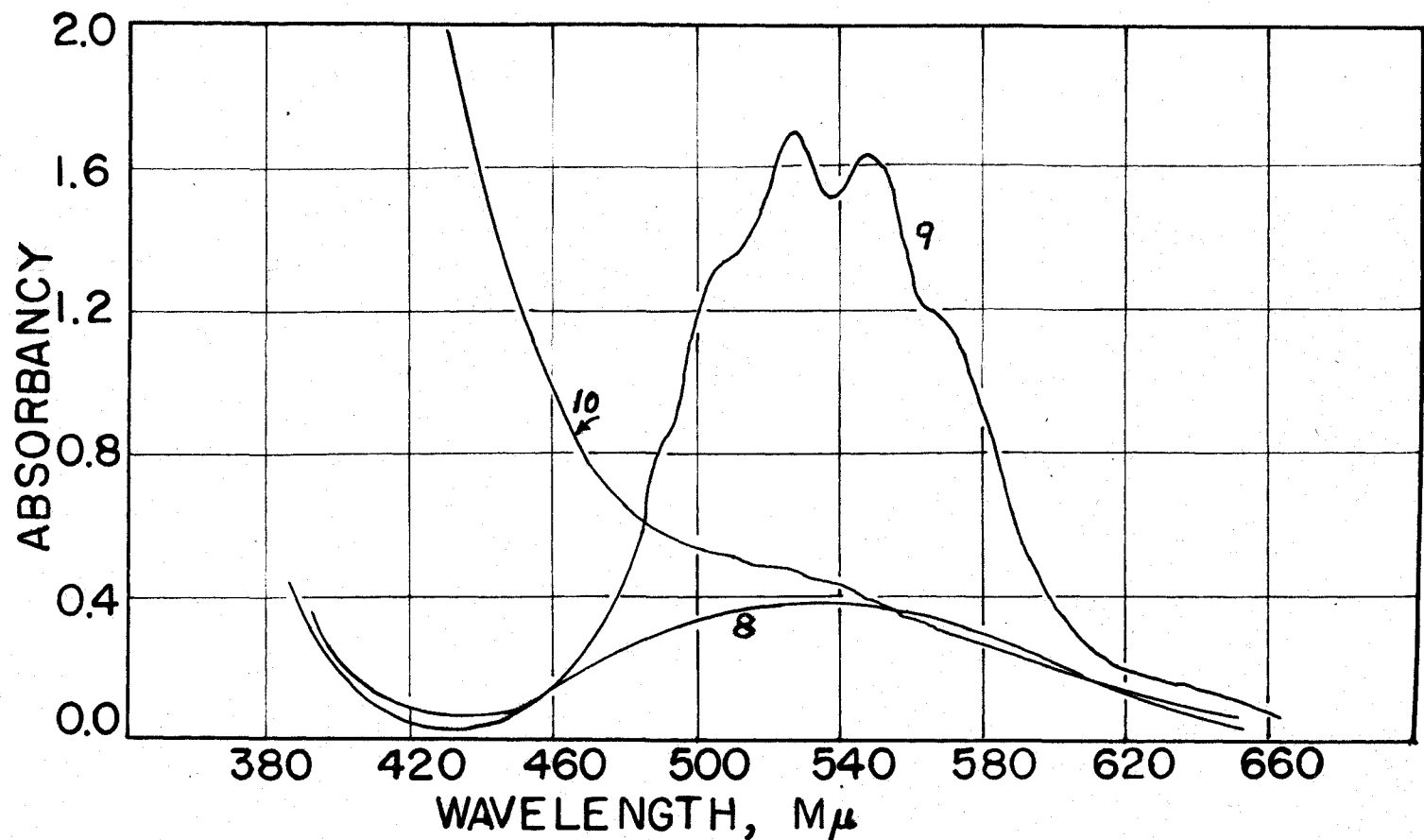
Figure 2. Absorption Characteristics of Aqueous Solutions of Various Manganese Oxidation States on the Cary Spectrophotometer. Curves: 8, Mn^{III} with Low Mn^{II} Concentration; 9, Permanganate; 10, Manganese(IV) with Low Permanganate.

consist of numerous trial and error attempts to fit absorbancy indices to the data at hand, and the most advantageous starting point was not obvious. It was decided to use first the data obtained for manganese(IV)-permanganate solutions since these samples contained no manganese(II), the colorless species which was not measurable directly. Curve 10, Figure 2, was an example of a plot for such a sample with low permanganate content. The slight irregular rise due to permanganate was approximately 0.026 absorbancy units at 526 $m\mu$. The molar absorbancy index for this species is 2241 $\pm$ 5 at 5260 $\overset{o}{A}$ as reported by Hayes (49). Since the measurements were made using a 5 cm. cell, the absorbancy was divided by five times the absorbancy index to obtain a concentration of 0.023×10^{-4} M. When this concentration was subtracted from the total manganese concentration of 2.84×10^{-4} M, a value of 2.82×10^{-4} M was obtained for Mn^{IV}. The absorbancy at 430 $m\mu$ of 1.926 units was assumed due to the Mn^{IV} content alone since permanganate has a low absorbancy index at that wavelength and the concentration of the latter was quite low. An absorbancy index of 1370 was calculated for manganese(IV) at 430 $m\mu$; for a series of similar curves, values of 1360 and 1380 were obtained with an average of 1370 $\pm$ 7. From this same set of curves, the absorbancy index for manganese(IV) at 526 $m\mu$ was estimated to be about 325. These values were then used in the calculations for Mn^{III}-Mn^{IV} curves to obtain

absorbancy indices for manganese(III). Several values were
tried for the manganese(IV) absorbancy index at 526 mμ, but
the most consistent results were obtained when 320 was used.
The results of the calculations, as shown in Table 1, indi-
cated an absorbancy index of 101 $\pm$ 3 for manganese(III) at
526 mμ.

The absorbancy indices obtained above were checked on
several curves, and the sum of the concentrations of the
various species calculated in this manner equaled the total
manganese content as determined colorimetrically. It was
necessary that the solutions examined by this method contained
only manganese(III) and manganese(IV) or permanganate and
manganese(IV). Since the equilibrium constant for the dis-
proportionation of manganese(III) is very small, the concen-
tration of manganese(II) ion in solutions containing appreci-
able manganese(III) and some manganese(IV) was effectively
zero. All of the manganese(IV) solutions used in the titra-
tions were analysed by taking absorbancy readings at 430 and
526 mμ and utilizing the absorbancy indices determined by the
preceding method. In addition the total manganese content
was determined colorimetrically using the periodic acid oxi-
dation procedure.

Table 1

Extinction Coefficient Data

Curve number in Fig. 1	Absorbancy 430 mμ	$[Mn^{IV}]$ X 10⁴ moles/Liter	Mn^{IV} Absorbancy at 526 mμ	Absorbancy 526 mμ	$[Mn^{VII}]$ Total X 10⁴ moles/Liter	Absorbancy index Mn^{III} at 526 mμ
1	0.050	0.365	0.012	0.120	11.2	100
2	0.335	2.45	0.079	0.172	11.2	106
3	0.700	5.11	0.163	0.220	11.2	94
4	0.962	7.02	0.222	0.267	11.2	107
5	1.342	9.79	0.313	0.410	19.3	102
	0.190/5	0.278	0.444/5	0.782/5	7.3	97
	0.141/5	0.206	0.329/5	0.560/5	4.6	104
	0.055	0.40	0.013	0.203	19.4	100
	0.718	5.24	0.168	0.312	19.3	103
						101

F. Method

Since the manganese(III) and manganese(IV) species were colored, spectrophotometric methods were employed to study the rapidity with which the manganese(II), (III), (IV) equilibrium was established. When an amber or brown manganese(IV) solution was mixed with a colorless manganese(II) solution, the tervalent manganese formed was violet. The change in absorbancy at 526 mμ indicated the combined variation of the manganese(III) and manganese(IV) concentrations; the decrease in the concentration of the quadrivalent species could be followed at 430 mμ. By locking the scanning mechanism of the

Cary Recording Spectrophotometer and allowing the chart to proceed, the change in absorbancy with time was recorded at any selected wavelength.

Qualitative visual examination of color change when the divalent and quadrivalent species were mixed indicated that manganese(III) formed rapidly. However, by keeping the time of mixing to a minimum, it was hoped that any small change near the end of the reaction not observable to the eye would be determined. The general procedure followed was to half fill a sample cell with a solution of manganese(II) and then rapidly add manganese(IV) solution up to the bottom of the neck of the cell leaving an air space between the solution and the stopper to facilitate mixing. The cell was stoppered, shaken, and placed in the sample chamber of the spectrophotometer. The chart mechanism was actuated during the addition of the second solution to the cell, and the time elapsed between the starting of the chart and the first absorbancy reading was usually ten to fifteen seconds. No change in absorbancy was found at either wavelength over a thirty minute period; the equilibrium had been established in less than ten seconds at room temperature. Since part of this elapsed time was required for mixing the reactants, the reaction was undoubtedly completed in a much shorter period, and the equilibrium was considered to be rapidly established under the conditions of the experiments.

After the determination of the absorbancy indices for the manganese species at two wavelengths, the most obivous method for determining the equilibrium concentrations was also a direct calorimetric procedure. From absorbancy readings at 430 mμ and 526 mμ and from total manganese determinations, the concentrations of each species should be obtainable.

Two methods were tested to determine the equilibrium constant from colorimetric measurements. In the first procedure, iodic acid solutions which contained high relative concentrations of manganese(III) iodate were shaken with solid manganese(II) iodate for long periods to ensure saturation with the divalent species. Absorbancy measurements at 430 mμ and 526 mμ were made, and the total manganese concentrations were determined colorimetrically. The manganese concentration in the solution was then reduced to a definite fraction of its original value by dilution with iodic acid; all solutions used in any series of experiments were of the same iodic acid concentration. The diluted solutions were shaken with the same manganese(II) solid used previously. After absorbancies had been measured, the procedure was repeated. In this method the manganese(II) iodate and the iodic acid concentrations remained constant. In addition possible errors due to impurities in the manganese(II) solid were reduced by using the same sample to saturate each solu-

tion. To determine the manganese(II) concentration more accurately, iodic acid which contained no tervalent manganese was saturated with the divalent species in a similar manner, and the total manganese content was determined. From these data the concentrations of each of the manganese species was calculated.

As discussed previously, decomposition of manganese(II) solutions occurred if they were allowed to stand for long periods of time. It was possible that such decomposition was taking place during the long shaking periods required to ensure saturation with manganese(II). Consequently a more rapid procedure involving no solid-solution equilibrium was indicated.

In the second method tried, equilibrium solutions of manganese(II), (III), (IV) in iodic acid were diluted to known volumes with iodic acid which contained manganese(II). Absorbancies at 430 mμ and 526 mμ were measured to obtain the manganese(III) and (IV) concentrations, and total manganese was determined. The manganese(II) was then calculated by difference. Equilibrium constants calculated from this data were erratic also. It was apparent that the sensitivity of the direct colorimetric procedure was insufficient to obtain good results.

An examination of the probable magnitude of the terms in the equilibrium constant showed that K_c had to be fairly small to be measurable by colorimetric methods. For example,

in 1 M iodic acid the saturation concentration of manganese(II) was approximately 1.8 X 10⁻⁴M; manganese(III) concentrations varied but an average value of 5.0 X 10⁻⁴M was used for this calculation. The error in reading the Beckman spectrophotometer (40) as discussed under apparatus description was about 0.5% for absorbancies of 0.500 or an error in reading of approximately 0.0025 units. An absorbancy of 0.0025 at 430 mµ corresponded to a manganese(IV) concentration of 1.8 X 10⁻⁶M. For a K_c of 750, the manganese(IV) concentration was given by the following relationship:

$$[Mn^{IV}] = \frac{[Mn^{III}]^2}{[Mn^{II}]K_c} = \frac{(5.0 \times 10^{-4})^2}{(1.8 \times 10^{-4})(750)} = 0.0185 \times 10^{-4}. \tag{19}$$

For an error of less than 25%, the magnitude of the equilibrium constant had to be 150 or less.

The colorimetric methods indicated that the equilibrium constant was sufficiently large under the conditions of the experiment to make the measurement of its magnitude impossible by spectrophotometric procedures. However, in the determination of equilibrium constants from cell potentials, as reported by Grube and co-workers (12, 26), a large constant and the corresponding large potential difference was advantageous. A suitable reference electrode, the silver-silver iodate half cell, was available, and the reaction between the three manganese species was sufficiently rapid that it was admirably suited to titration techniques. There-
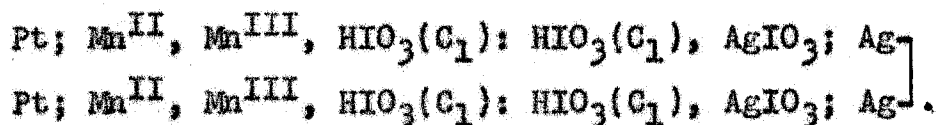
fore the potentiometric procedure was used finally for the determination of the equilibrium constant.

In the method described by Grube and co-workers the potentials were determined for solutions of equal manganese(II) and manganese(III) concentrations and equal manganese(III) and manganese(IV) concentrations. The results were only as accurate as the measurement of the two potentials and the preparation of the two solutions. By following through the complete titration curve, a series of potential values would indicate any erratic trends in the potentials. Since the preparation and analysis of the manganese solutions was complicated, it was advantageous that the endpoint in the potentiometric titration could be used to verify concentrations determined colorimetrically. In addition all measurements were made on essentially one solution instead of two.

The general procedure followed was to add small amounts of a manganese(III), (IV) iodate solution from a microburet to a rapidly stirred solution of manganese(II) iodate contained in a small beaker. In any one titration the solution added from the buret matched exactly the iodic acid, perchloric acid, and lithium perchlorate concentrations, and accordingly the ionic strength, of the solution in the titration vessel. It should be noted that the total volume of the additions of solution in the titration were relatively large. In a limited number of cases the procedure was reversed and

the manganese(II) iodate was used as the titrating solution. The end results obtained using either procedure were identical, and no curves of the latter type are included here.

Potential measurements were made using a Beckman model G pH meter after each addition of titrating solution. The cell used, as discussed in the appendix, was of the following type:

Pt; Mn^{II}, Mn^{III}, $HIO_3(C_1)$: $HIO_3(C_1)$, $AgIO_3$; Ag⌐
Pt; Mn^{II}, Mn^{III}, $HIO_3(C_1)$: $HIO_3(C_1)$, $AgIO_3$; Ag⌐.

Temperature control was attained by placing the reaction vessel in a water bath thermostat. Variation in the temperature of the reactants did not exceed $\pm 0.2^\circ$ even at the higher temperatures used. The titrating solution was added in sufficiently small increments that no sudden changes in temperature were observed; in addition the large number of potentials measured in this manner permitted the plotting of smooth titration curves.

Preliminary experiments showed that the equilibrium state was dependent upon temperature, acidity, and iodate concentration. In addition the usable concentration range for the manganese(III), (IV) solution was determined. After these facts were obtained, the various conditions to collect experimental data were outlined.

The general method of investigation was to keep certain variables essentially constant while changing one or two

others. Hydrogen ion, manganese, iodate, iodic acid, and
temperature were all variables to be considered. The titra-
tions were made using the methods described previously, and
the conditions for each are given in Table 2. In each case
the titrations were carried out in duplicate or triplicate.
The experiments numbered one to six inclusive were made with
temperature the main variable. Experiments numbered seven
through fifteen inclusive were made to determine the tempera-
ture dependence at three iodic acid concentrations. The re-
sults of the entire set of experiments, numbered one through
fifteen inclusive, show the dependence of the equilibrium on
the iodic acid concentration at several temperatures. Repre-
sentative titration curves from each experiment were plotted
as shown by the smooth curves in Figures 3 through 8.

The effect of varying manganese concentrations was
studied during these first experiments. In making duplicate
or triplicate titrations, the manganese concentration was
changed between determinations, but no change in the equilib-
rium constant was evident. Negative results were obtained
for eight such duplicate titrations on separate samples; it
was concluded that there was no manganese dependence and that
no polymerization or association of the manganese was occur-
ring in the iodate solutions. If no polymerization occurred,
it was apparent from the equation for the equilibrium constant
that the equilibrium state for a particular set of conditions

was independent of the volume.

In experiments one to fifteen inclusive no attempt was made to isolate the effect due either to the hydrogen ion or the iodate ion concentration. The ionic strength was also permitted to vary. Attempts to isolate the iodate dependence by using lithium iodate in neutral solutions were unsuccessful. It was found by qualitative visual tests that a hydrogen ion concentration of approximately 0.07 M was required before the violet manganese(III) color would appear in the titrations. No potential break was observed in the titration curve for the neutral solutions. Consequently it was necessary to keep the hydrogen ion concentration sufficiently high that it remained about constant during the studies on iodate dependence.

In experiments fifteen to twenty-five inclusive the ionic strength was kept essentially constant using lithium perchlorate, and the effect of the iodate ion was studied separately at three hydrogen ion concentrations. In the experiments numbered sixteen through nineteen the hydrogen ion concentration was maintained effectively constant for several iodic acid concentrations by making the solutions 2 M in perchloric acid. In experiments twenty to twenty-three inclusive and in twenty-four the hydrogen ion was fixed by using 1 M and 1.5 M perchloric acid respectively. These titrations were carried out at $23.4^{\circ}C$. From the series of curves,

sixteen through twenty-four, the hydrogen ion dependence could be calculated. Representative experimental curves were plotted and are given in Figures 9 through 11. In experiment twenty-five at 0.0°C the hydrogen ion concentration was maintained at 2 M with perchloric acid in a 1 M iodic acid solution. This experiment corresponded to number sixteen except for the difference in temperature. Figure 12 shows the results of this experiment.

The nature of the complexes in solution was investigated to a limited extent by observing the movement of the manganese(III) and manganese(IV) species during electrolysis. A violet solution containing essentially Mn^{III} in 1 M iodic acid was placed in the bottom of a U tube and 1 M iodic acid was carefully added to each arm of the tube in such a manner that the colored solution was left undisturbed. A visible boundary existed between the violet solution and the colorless acid. Platinum electrodes were inserted into the top solutions in each side of the tube, and a direct current of 0.5 milliamperes was passed through the cell for two hours. The boundaries were observed to move toward the anode and away from the cathode. The procedure was repeated using a brown solution containing essentially manganese(IV) in iodic acid and lithium iodate. Similar results were obtained; the boundaries moved away from the cathode and toward the anode. It was concluded that both the manganese(III) and manganese(IV) species were negatively charged.

Table 2

Solution Strengths and Temperatures for the Potentiometric Titrations

Experiment	M_{HIO_3}[a]	M_{MnII} X 10^4	M_{HClO_4}	$M_{MnIII MnIV}$ X 10^4	M_{LiClO_4}	Temperature °C
1	0.990	1.84	0.000	8.45	0.000	0.0
	0.990	1.84	0.000	5.30	0.000	0.0
2	0.990	1.84	0.000	5.30	0.000	23.4
	0.990	1.84	0.000	5.30	0.000	23.4
3	0.990	1.84	0.000	5.30	0.000	44.8
	0.990	1.84	0.000	5.30	0.000	44.8
4	0.990	1.84	0.000	6.80	0.000	24.3
	0.990	1.78	0.000	6.20	0.000	24.3
	0.990	1.78	0.000	6.20	0.000	24.3
5	0.990	1.78	0.000	6.20	0.000	57.2
	0.990	1.78	0.000	6.20	0.000	57.2
	0.990	1.78	0.000	6.20	0.000	57.2
6	0.497	1.70	0.000	8.28	0.000	0.0
	0.497	1.70	0.000	3.10	0.000	0.0
7	0.497	1.70	0.000	3.10	0.000	22.5
	0.497	1.70	0.000	3.10	0.000	22.5
8	0.497	1.70	0.000	3.10	0.000	43.5
	0.497	1.70	0.000	3.10	0.000	43.5
9	0.497	1.70	0.000	3.10	0.000	61.5
	0.497	1.70	0.000	3.10	0.000	61.5
10	1.782	2.04	0.000	6.65	0.000	0.0
	1.782	2.04	0.000	6.65	0.000	0.0
11	1.782	2.04	0.000	6.65	0.000	47.3
	1.782	2.04	0.000	6.65	0.000	47.3
12	1.782	2.04	0.000	6.65	0.000	22.8
	1.782	2.04	0.000	6.65	0.000	22.8
13	1.782	2.04	0.000	6.65	0.000	64.5
	1.782	2.04	0.000	6.65	0.000	64.5
14	0.249	1.02	0.000	2.78	0.000	0.0
	0.249	1.02	0.000	2.78	0.000	0.0

[a]M refers to molar concentration.

Table 2

(Continued)

| Experiment	$M_{HIO_3}^a$	$M_{Mn\,II}$ X 10⁴	M_{HClO_4}	$M_{Mn\,III}Mn\,IV$ X 10⁴	M_{LiClO_4}	Temperature °C
15	0.249	1.02	0.000	2.78	0.000	21.5
	0.249	1.02	0.000	2.78	0.000	21.5
16	1.000	1.80	2.000	6.67	0.000	23.4
	1.000	1.80	2.000	6.02	0.000	23.4
17	0.800	1.44	2.000	5.68	0.000	23.4
	0.800	1.44	2.000	3.23	0.000	23.4
18	0.640	1.66	2.000	5.66	0.000	23.4
	0.640	1.66	2.000	4.54	0.000	23.4
19	0.500	1.44	2.000	3.32	0.000	23.4
	0.500	1.44	2.000	3.00	0.000	23.4
20	1.000	1.80	1.000	6.25	1.000	23.4
	1.000	1.80	1.000	6.25	1.000	23.4
21	1.000	1.80	1.000	6.25	1.000	23.4
	0.800	1.44	1.000	5.00	1.000	23.4
	0.800	1.44	1.000	5.00	1.000	23.4
22	0.640	1.15	1.000	4.00	1.000	23.4
	0.640	1.15	1.000	4.00	1.000	23.4
23	0.500	0.90	1.000	3.12	1.000	23.4
	0.500	0.90	1.000	3.12	1.000	23.4
24	1.000	1.60	1.500	6.60	0.500	23.4
	1.000	1.60	1.500	6.60	0.500	23.4
	1.000	1.60	1.500	6.36	0.500	23.4
25	1.000	1.56	2.000	6.40	0.000	00.0
	1.000	1.56	2.000	6.40	0.000	00.0

^{a}M refers to molar concentration.
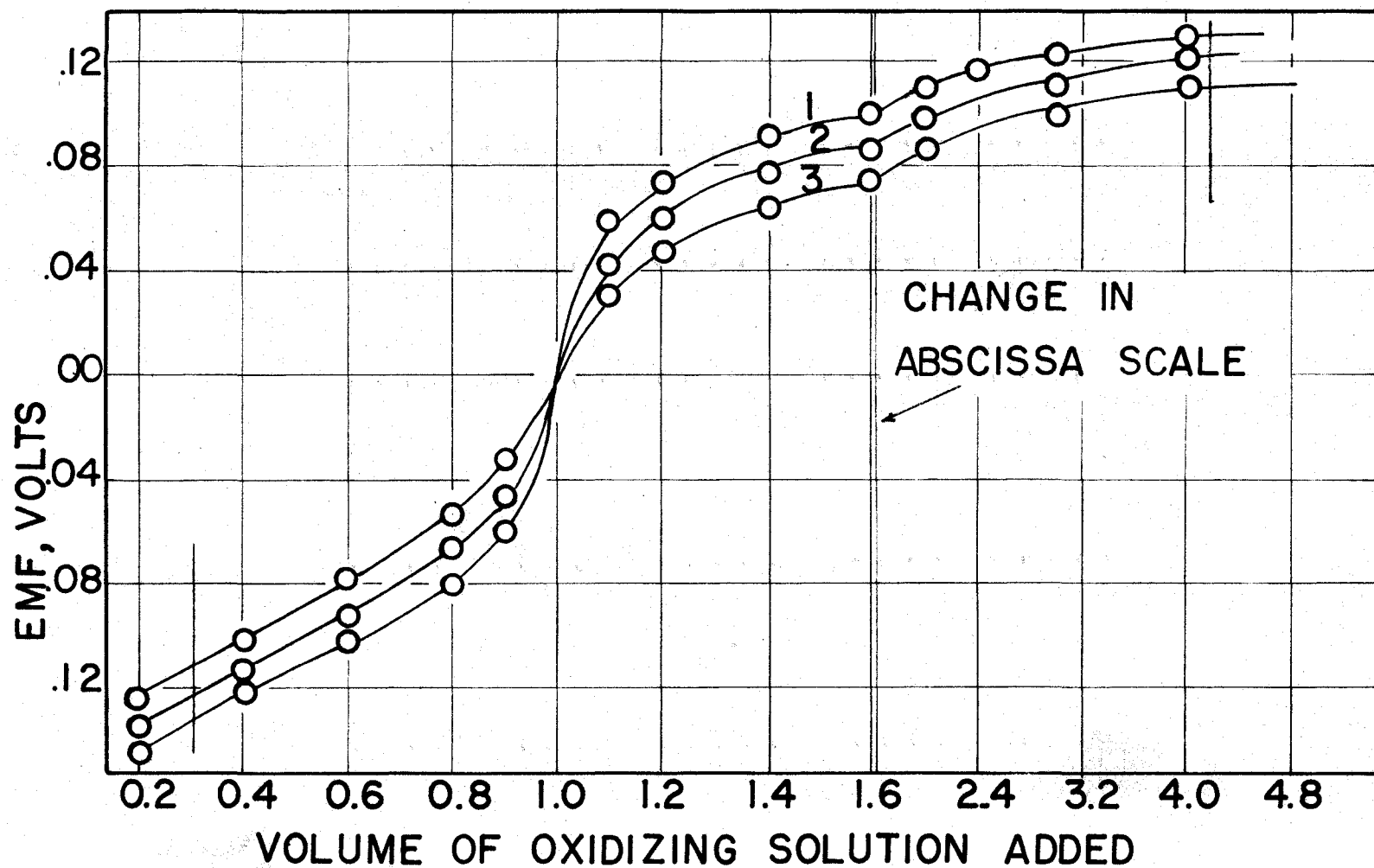
Figure 3. Potentiometric Titration Curves of Manganese(II) by Manganese(III), (IV) Solutions in 0.990 M iodic acid. Curves: 1, 0.0°C; 2, 23.4°C; 3, 44.8°C.
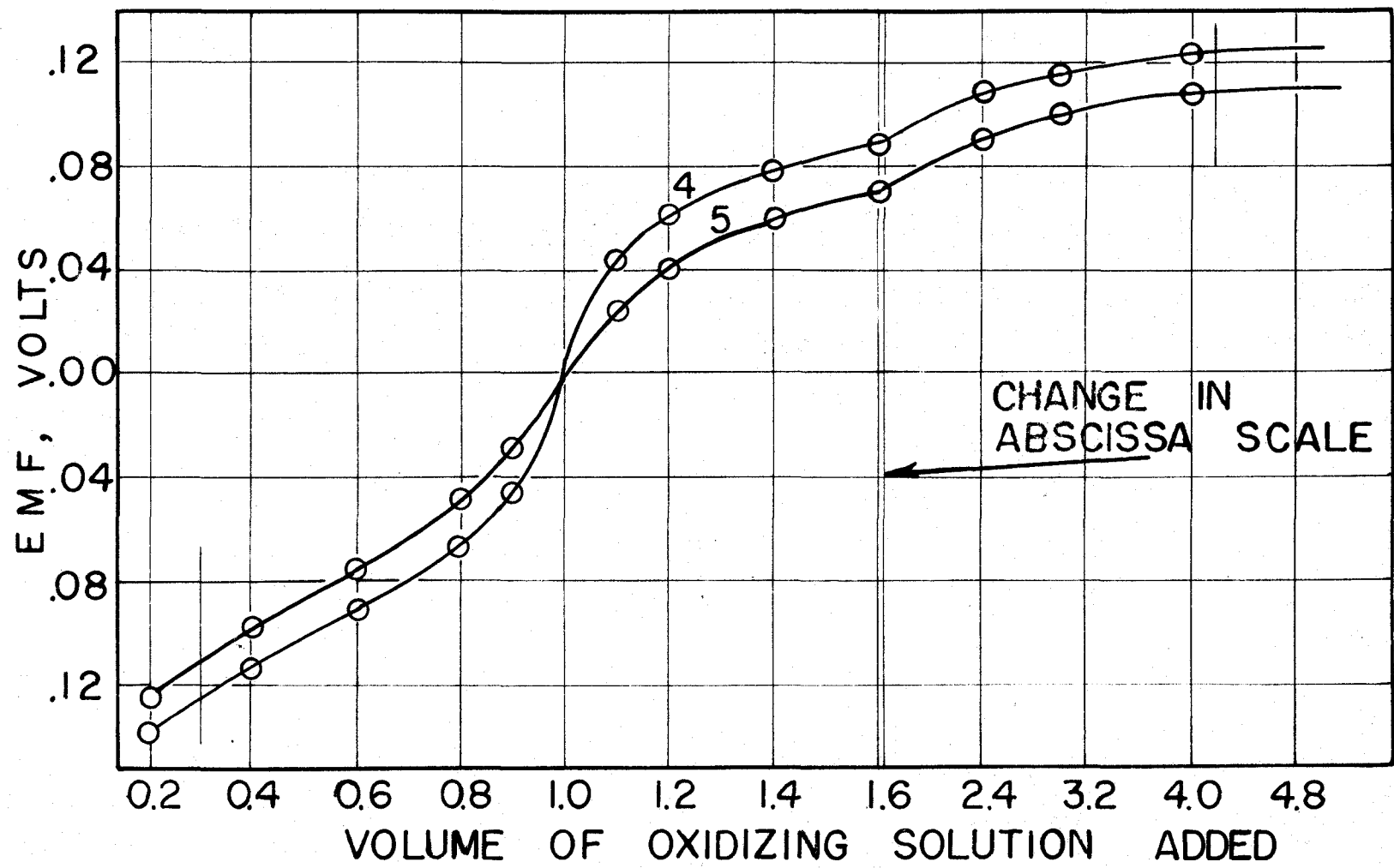
Figure 4. Potentiometric Titration Curves of Manganese(II) by Manganese(III), (IV) Solutions in 0.990 M Iodic Acid. Curves: 4, 24.3°C; 5, 57.2°C.
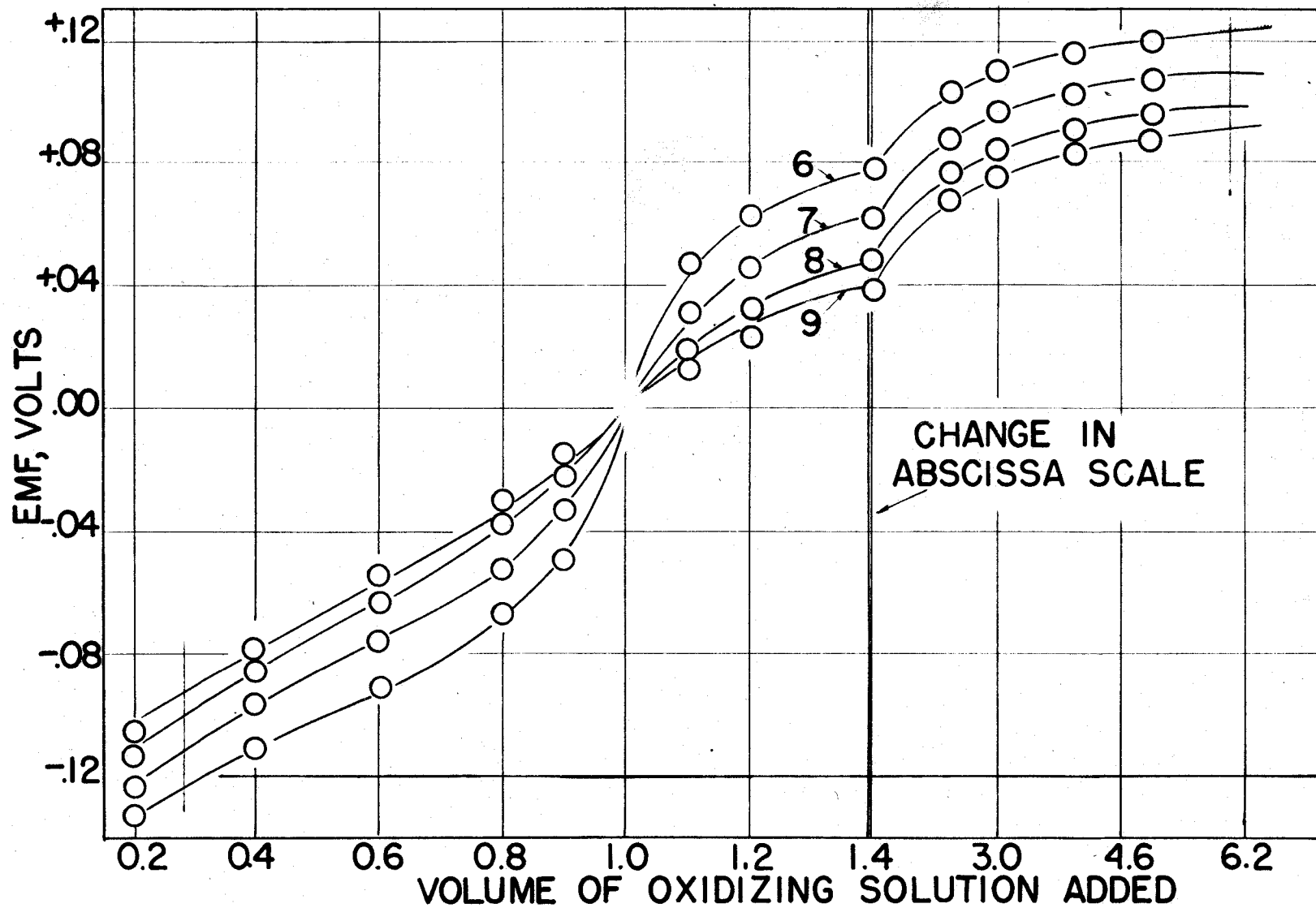
Fig. 5. Potentiometric Titration Curves of Manganese(II) by Manganese(III), (IV) Solutions in 0.497 M Iodic Acid. Curves: 6, 0°C; 7, 22.5°C; 8, 43.5°C; 9, 61.5°C.

Figure 6. Potentiometric Titration Curves of Manganese(II) by Manganese(III), (IV) Solutions in 1.782 M Iodic Acid. Curves: 10, 0.0°C; 11, 47.3°C.

CHANGE IN
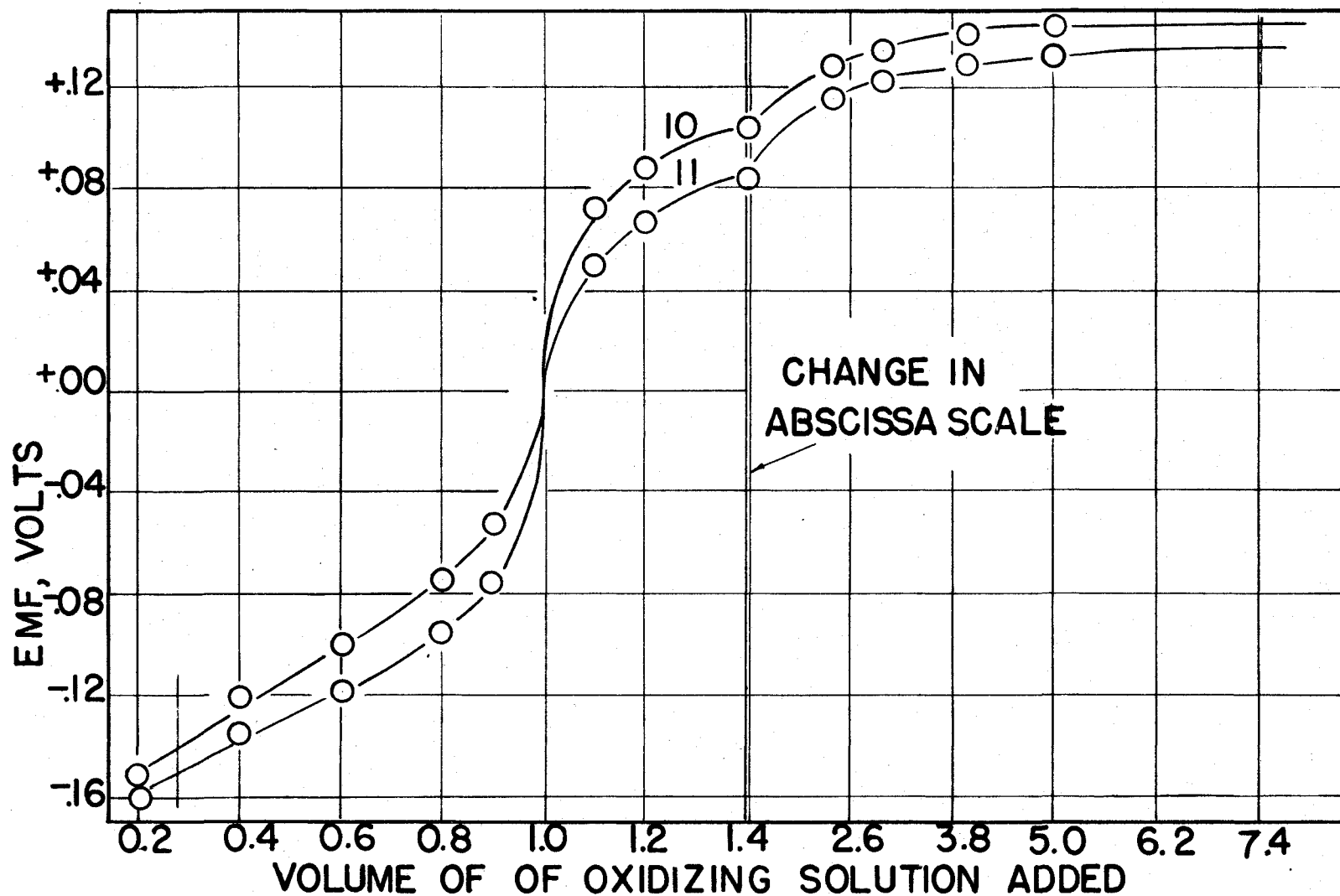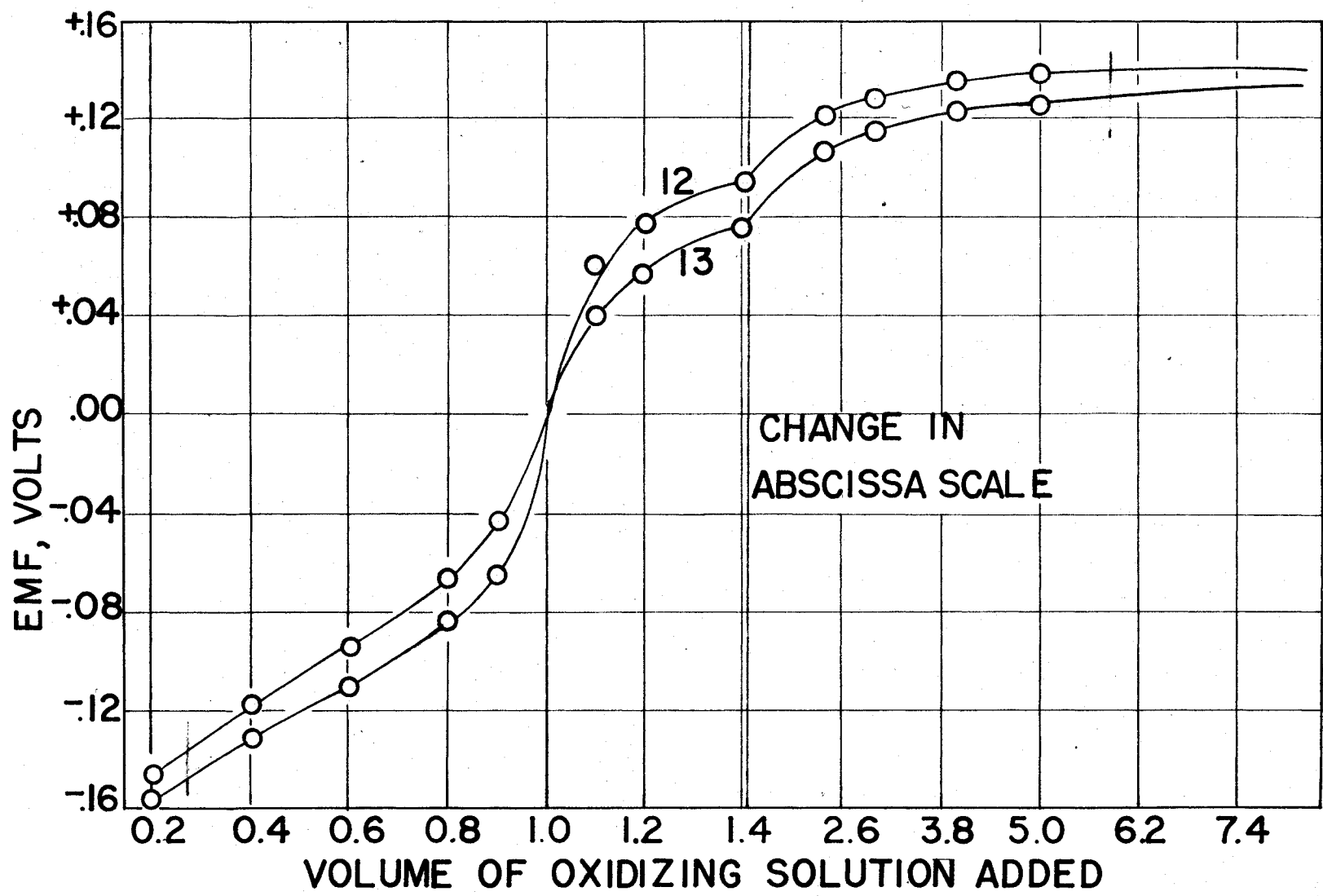ABSCISSA SCALE

Figure 7. Potentiometric Titration Curves of Manganese(II) by Manganese(III),
(IV) Solutions in 1.782 M Iodic Acid. Curves: 12, 22.8°C; 13, 64.5°C.
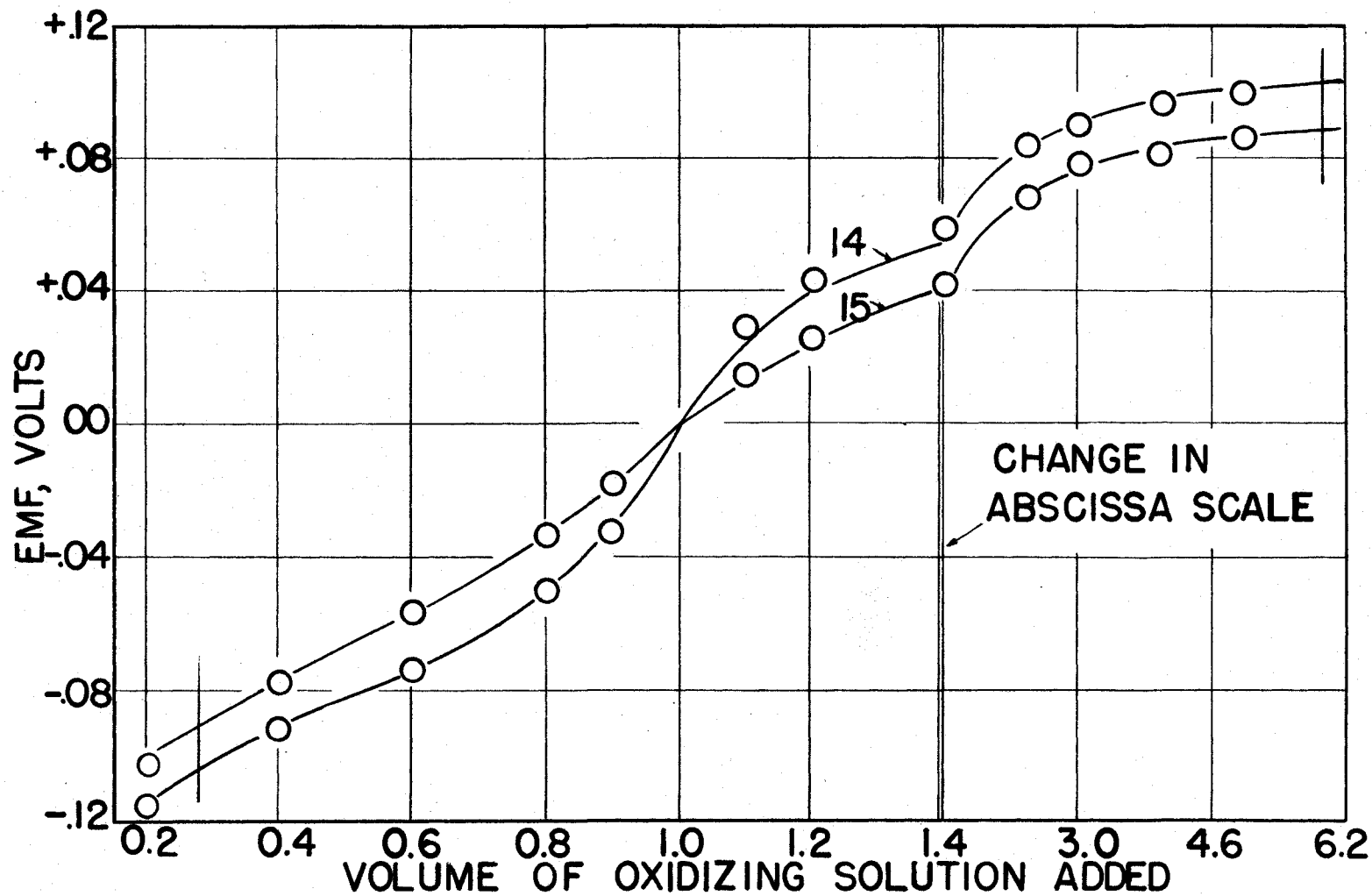
Figure 8. Potentiometric Titration Curves of Manganese(II) by Manganese(III), (IV) Solutions in 0.249 M Iodic Acid. Curves: 14, 0.0°C; 15, 21.5°C.

Figure 9. Potentiometric Titration Curves of Manganese(II) by Manganese(III), (IV) Solutions in 2 M Perchloric Acid at 23.4°C. Curves: 16, 1.00_0 M HIO_3; 17, 0.80_0 M HIO_3; 18, 0.64_0 M HIO_3; 19, 0.50_0 M HIO_3.

Figure 10. Potentiometric Titration Curves of Manganese(II) by Manganese(III), (IV) Solutions in 1 M Perchloric Acid and 1 M Lithium Perchlorate. Curves: 20, 1.00_0 M HIO_3; 21, 0.80_0 M HIO_3; 22, 0.64_0 M HIO_3; 23, 0.050_0 M HIO_3.

Figure 11. Potentiometric Titration Curve of Manganese(II) by Manganese(III),
(IV) Solutions in 1.5 M Perchloric Acid, 0.5 M Lithium Perchlorate,
and 0.80_0 M Iodic Acid at 23.4°C.
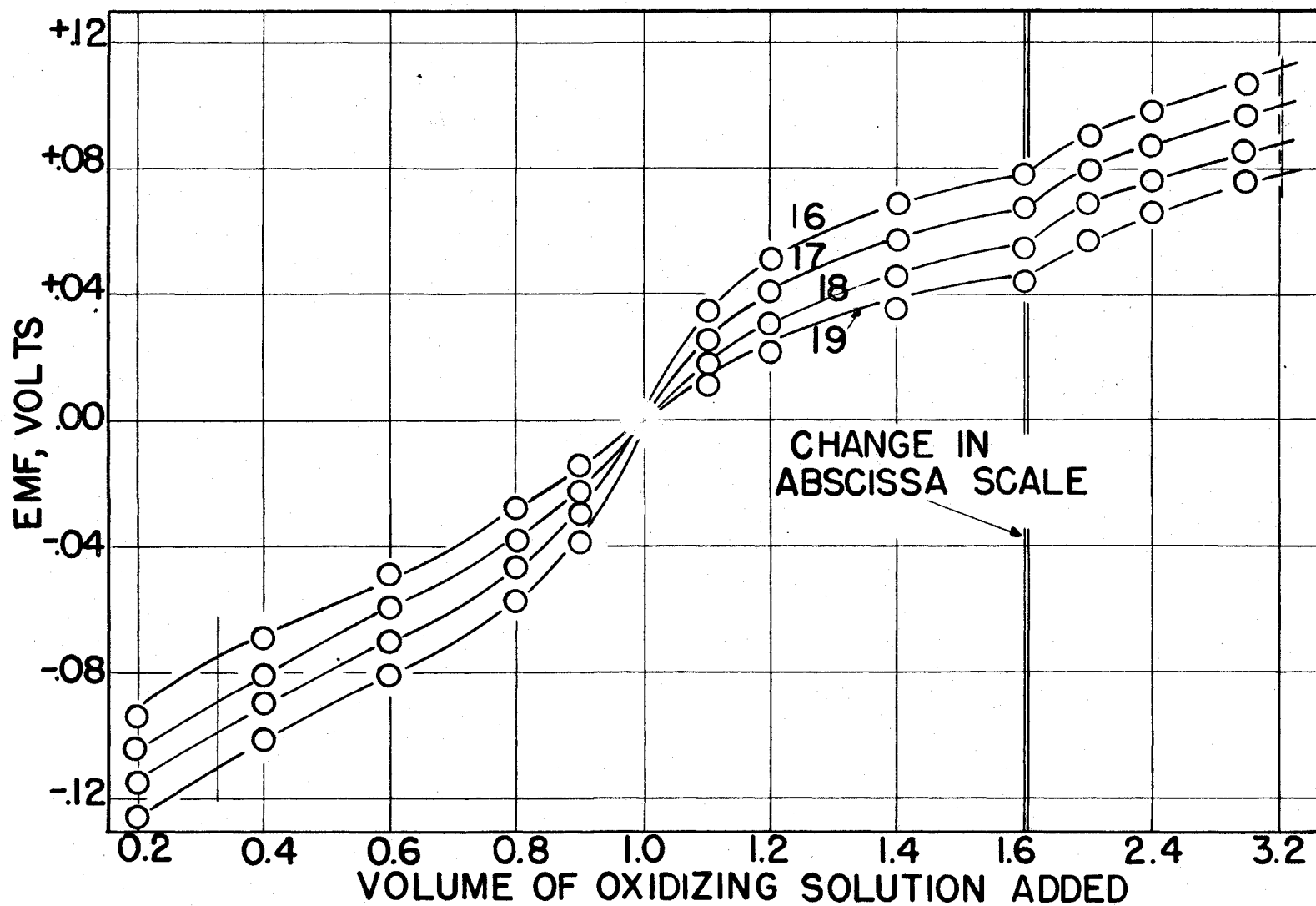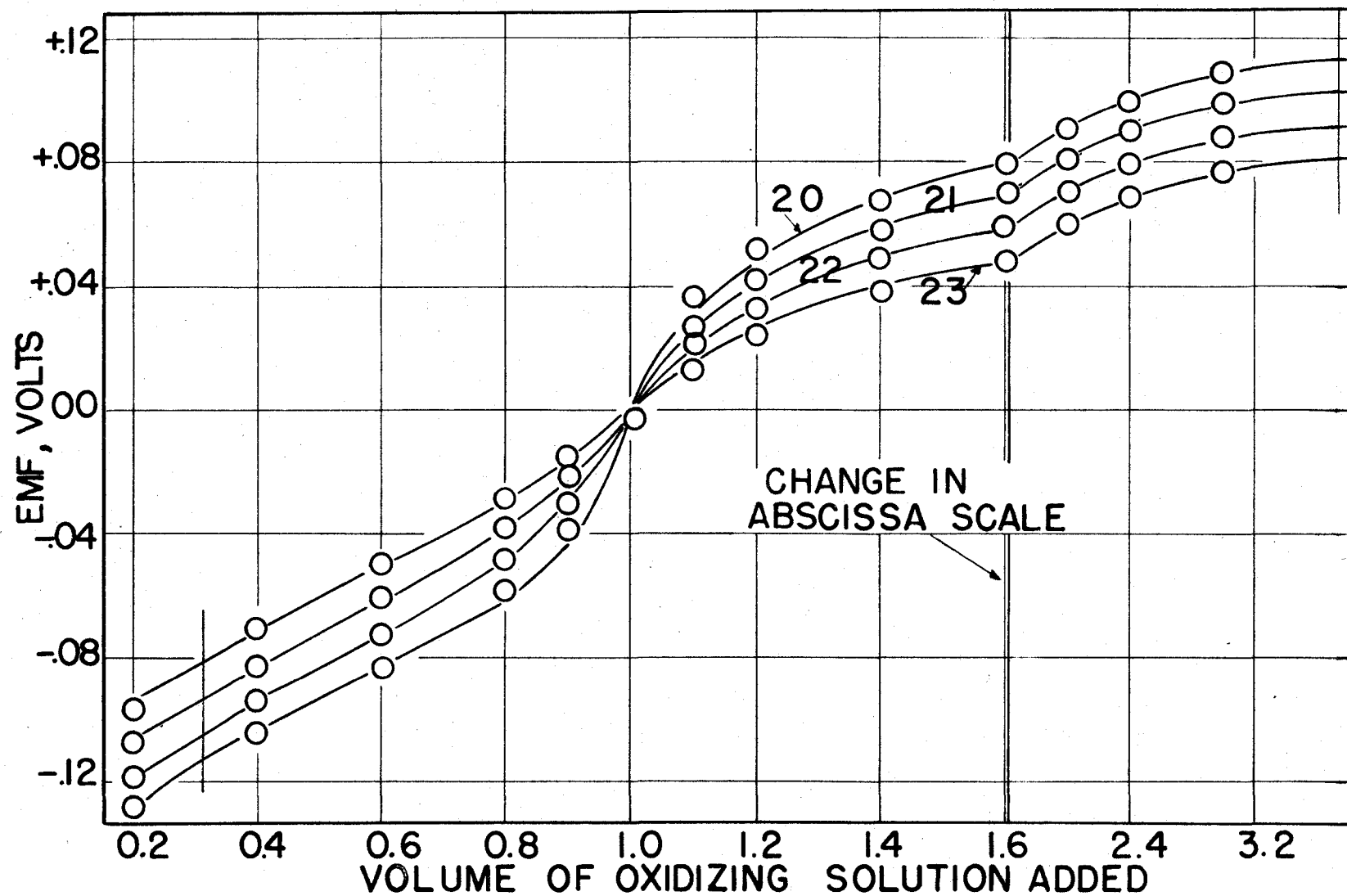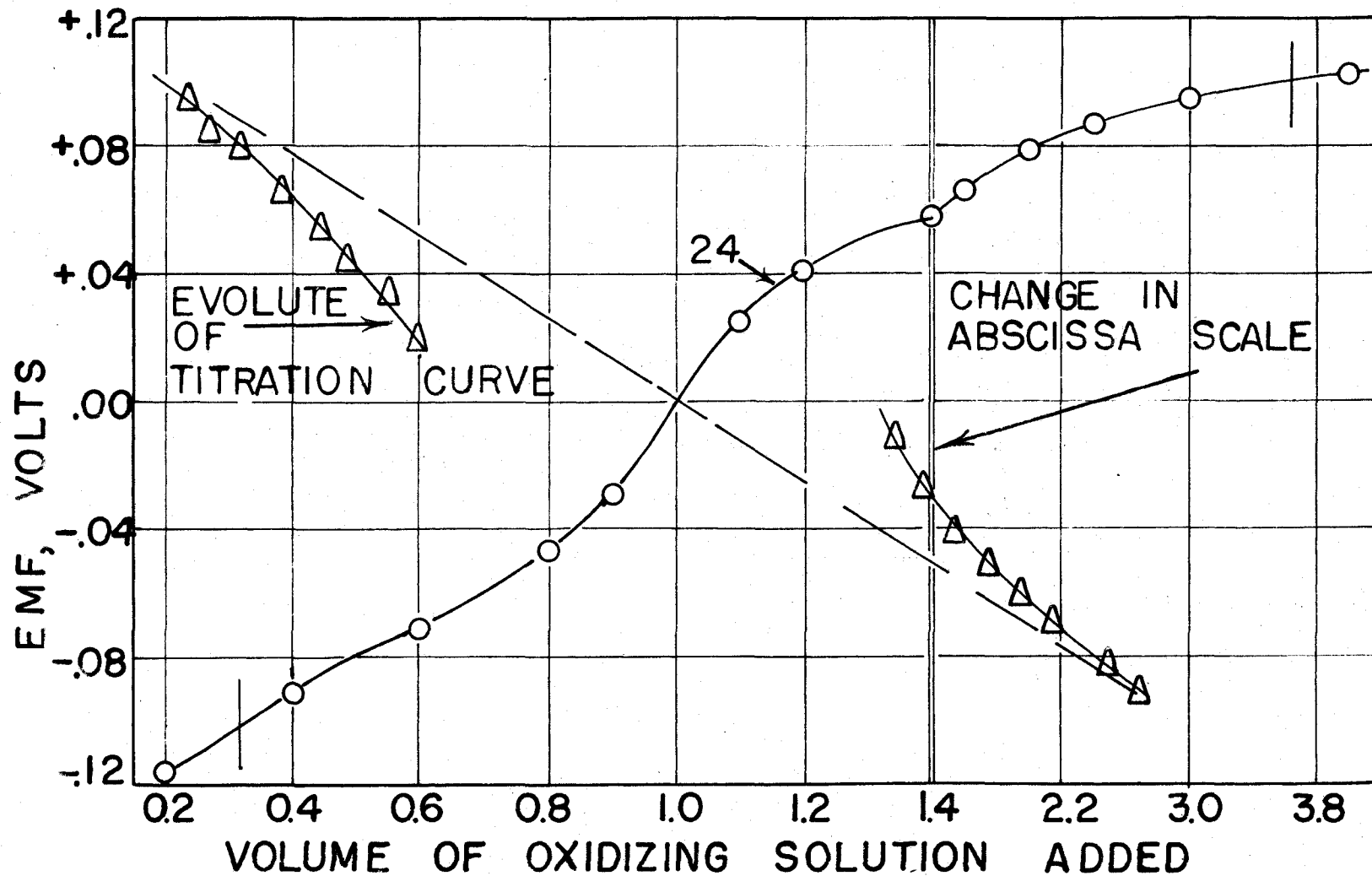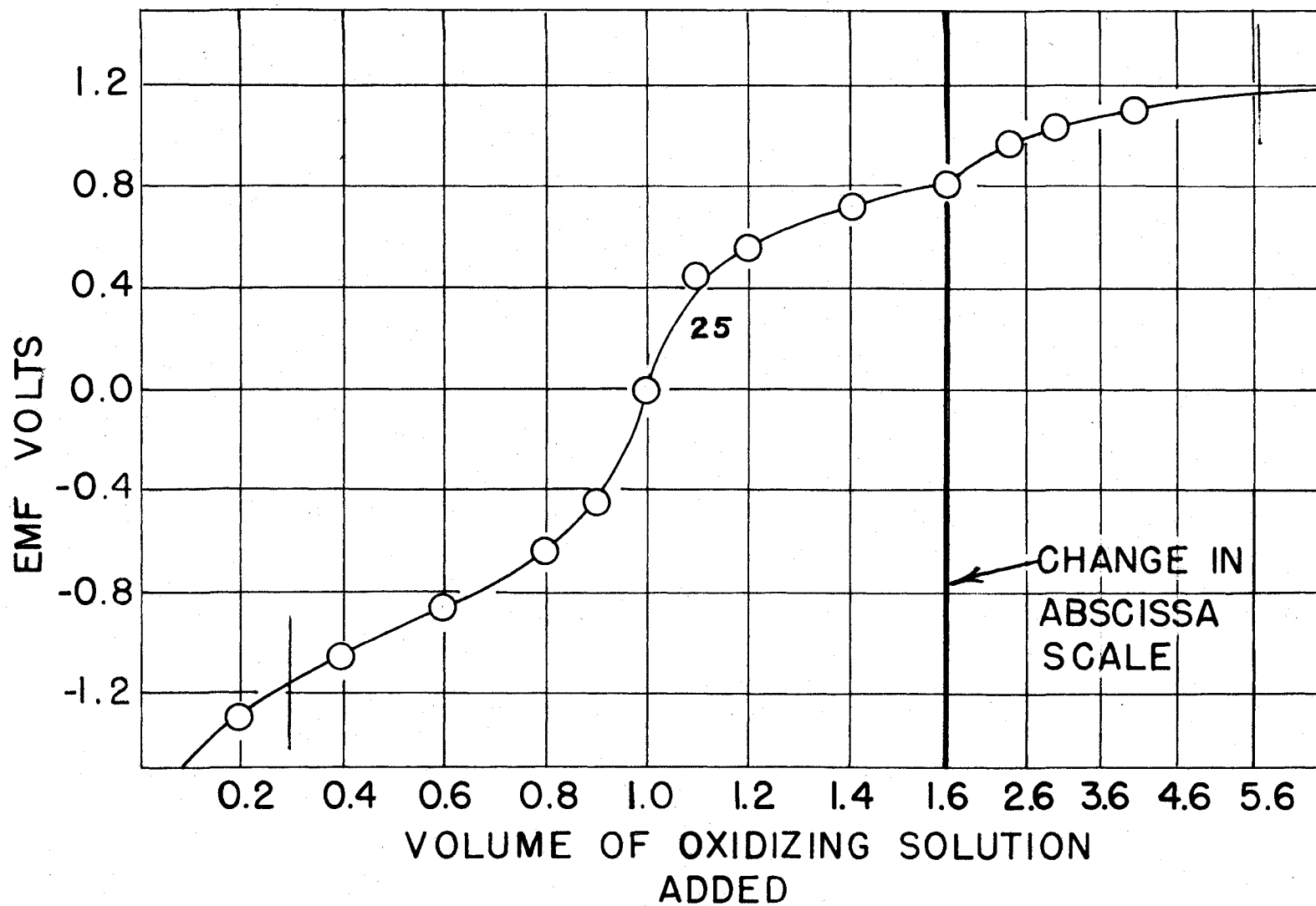
Figure 12. Potentiometric Titration Curve of Manganese(II) by Manganese(III), (IV) Solutions in 2 M Perchloric Acid and 1.00_0 M Iodic Acid at 0^0C.

G. Appendix: The Silver Iodate Reference Electrode

During the first attempts to titrate manganese(IV) with manganese(II), a saturated calomel reference electrode was used. However, an immediate precipitation of $K_2Mn(IO_3)_6$ occurred leaving a colorless solution. It was decided to try an iodate electrode which would not react with the manganese and at the same time would eliminate the iodate-chloride liquid junction. Takacs (50) described a $Hg_2(IO_3)_2$ electrode, but due to the oxidizing action of iodate ion in acid solution, iodic acid solutions could not be used with mercury(II). Pearce and Wirth (51) described a reversible silver iodate electrode with a standard potential of 0.3563 V when used with 0.1M KIO_3 solution. Kolthoff and Lingane (52) calculated a potential of 0.3551 V with respect to the hydrogen half cell for this electrode from solubility measurements made on silver iodate. Since no reaction between the silver and the manganese solutions was observed and since this electrode had been shown to be reversible, the silver iodate half cell was used as a reference electrode.

Silver iodate was precipitated by slowly adding dilute iodic acid to a rapidly stirred silver nitrate solution. The precipitate was carefully washed with water, dissolved in concentrated ammonium hydroxide, and recrystallized. After drying, the product was stored in a colored bottle until used.

The half cell was constructed by sealing a one centimeter length of platinum wire in the bottom of a small pyrex test tube in such a manner that approximately two millimeters of the wire protruded inside of the tube. A paste of silver oxide and water was applied to the exposed platinum inside the tube, and after slow drying, this coating was decomposed to metallic silver by heating to $400^{\circ}C$ in a muffle furnace. This silverizing process was repeated several times to ensure complete coverage of the platinum wire. A thick paste of the purified silver iodate with iodic acid of the concentration used in the titration was added to fill the tube to a depth of five to ten millimeters. A plug of glass wool was placed on top of the silver iodate paste to prevent stirring effects. Iodic acid was used to fill the tube and the bridge.

Since the differences between two potential readings was of importance rather than the accurate determination of one value, a double cell of the following type was used:

$$Pt; Mn^{II}, Mn^{III}, HIO_3(C_1): HIO_3(C_1), AgIO_3; Ag$$
$$Pt; Mn^{II}, Mn^{III}, HIO_3(C_1): HIO_3(C_1), AgIO_3; Ag \,.$$
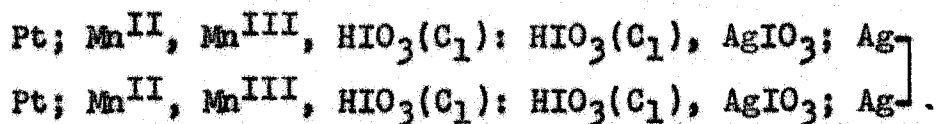
The total concentration of the manganese was relatively low compared to the acid molarity, C_1. Therefore the effect of the liquid junctions for this cell should have been very small although the concentrations of the manganese species varied over a wide range because a major fraction of the current was carried by the hydrogen and iodate ions present in

large excess. In addition the second junction potential in part cancels the first.

Prior to use two silver iodate electrodes were inserted in the same manganese iodate solution, the platinum leads were connected, and the cells left overnight to equalize. After this treatment, no potential difference was obtained for double cells of the above type when the same manganese solutions were used on each side.

New electrodes were prepared each time a titration was conducted in which a different iodic acid, lithium iodate, or perchlorate concentration was used. In the case of the titrations in perchlorate or lithium iodate solutions, the half cells and the bridge were prepared using similar solutions instead of iodic acid.

III. DISCUSSION AND RESULTS

From a cursory examination of the experimental curves, it seemed that the sharp breaks in the potential located the titration endpoints accurately. However, this was not the case. For titrations in which the overall change in potential was less than 0.200 volts, e.g. curves 14 and 15, a hurried estimation of the endpoint introduced errors of several millivolts. The curves were not symmetrical about the endpoint. A simple method for determining the endpoint with these asymmetrical curves was necessary.

In the classical method (53) the endpoint is determined by plotting the data and finding the point of inflection, by calculating the slope (dE/dv) of the titration curve as a function of volume and finding the volume corresponding to the maximum slope, or by calculating the second derivative (d^2E/dv^2) and determining the volume corresponding to a zero value. For asymmetrical curves the endpoint is likewise taken as the point of maximum slope.

Cavanagh (54, 55) suggested a special method for determining the endpoint based upon the mathematical behavior of the titration curve. He described an involved method for the calculation of the endpoint from two or more readings of the e.m.f. corresponding to suitable volumes of reagent.

Kolthoff (56) favors direct calculation of the endpoint from the strengths of the solution used. While this method

could have been used, no check or verification of the color-
imetric analyses would have been possible.

A graphical procedure described by Hahn and Weiler (57)
was used. In this method the evolute or locus of centers of
curvature of the experimental titration curve was constructed.
A straight line which was drawn asymptotically tangent to the
two branches of the evolute cut the original titration curve
at the endpoint. The authors showed by several examples that
this method was useful for curves of any or of unknown sym-
metry. The graphical construction required for this method
is illustrated in Figure 11.

After the endpoint for each titration curve had been
identified, the points at which the manganese(II) and manga-
nese(III) concentrations and the manganese(III) and manga-
nese(IV) concentrations were equal were still not evident.
Since the oxidizing solution is a mixture of two valence
states, these points of equal concentration had to be calcu-
lated for each different solution used. The colorless diva-
lent solutions were considered pure, and the concentration of
manganese(II) was determined colorimetrically by analytical
procedures already discussed. The concentrations of the ter-
and quadrivalent species in the oxidizing solutions were also
determined colorimetrically.

If the data for curve 1, Figure 3, is used in a sample
calculation, the method may be shown. The concentrations of

manganese(III) and manganese(IV) in the titrating solution were 1.48 X 10^{-4} M and 5.16 X 10^{-4} M respectively as determined from curve 26, Figure 13. Three milliliters of a 1.80 X 10^{-4} M manganese(II) solution was being titrated, and the endpoint of the titration occurred after the addition of 1.045 milliliters of the oxidizing solution which checked the concentrations determined colorimetrically. If Z was taken to be the milliliters of titrating solution added, the total amounts of the manganese species at any point in the titration were given by the following expressions if the equilibrium constant was large:

$$Mn^{II} = 5.40 \times 10^{-4} - 5.16 \times 10^{-4}Z \qquad (20)$$

$$Mn^{III} = 1.48 \times 10^{-4} + 2(5.16 \times 10^{-4})Z \quad . \quad (21)$$

Setting the two amounts equal and solving for Z, the equations reduced to:

$$Z = 5.40/ 16.96 = 0.318 \quad . \qquad (22)$$

Dividing this value of Z by 1.045 to convert to a scale in which the endpoint was at 1.00, the value for equal manganese(II) and manganese(III) concentrations was 0.304. For the other required point, the following equations were used:

$$Mn^{III} = 1.48 \times 10^{-4} + 2(1.045)(5.16 \times 10^{-4}) \qquad (23)$$

$$Mn^{IV} = (5.16 \times 10^{-4})(Z - 1.045). \qquad (24)$$

At equal concentrations,

$$Z = 16.18/ 3.68 = 4.39 . \qquad (25)$$

Converting to the above scale, the value became 4.20. Sim-

ilar calculations were made for each titration, and the
points of equal concentration were indicated by vertical
lines cutting the titration curves in Figures 3 to 12 inclu-
sive. The e.m.f. values at these points were read from the
curves, and the differences between the potentials for equal
manganese(II) and (III) and equal manganese(III) and (IV)
concentrations, ΔE, were calculated for each titration.
These data are given in Table 3. By using equation (10) and
the ΔE values, the equilibrium constants, K_c', were calculated;
these values are included in Table 3.

The entire titration curves were determined to avoid
using only two experimental points. However the K_c' values
were actually calculated from two points on each curve, and
the remainder of the curve was used only to determine the
endpoint and to observe any abnormal deviations in potential.
More satisfying results were attained by comparing the entire
experimental curves with theoretical curves the points of
which were calculated in the following manner.

If p was the original amount of manganese(II) being ti-
trated, m was the manganese(IV) added, and x, the Mn^{II} or
Mn^{IV} which had reacted, then the following equations applied:

$$Mn^{II} + Mn^{IV} \rightleftharpoons 2 Mn^{III} \qquad (26)$$
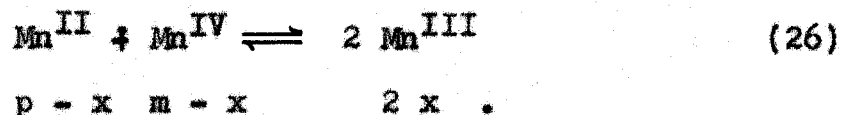
$$p - x \quad m - x \qquad 2 x \quad .$$

The concentration equilibrium constant for the reaction was,
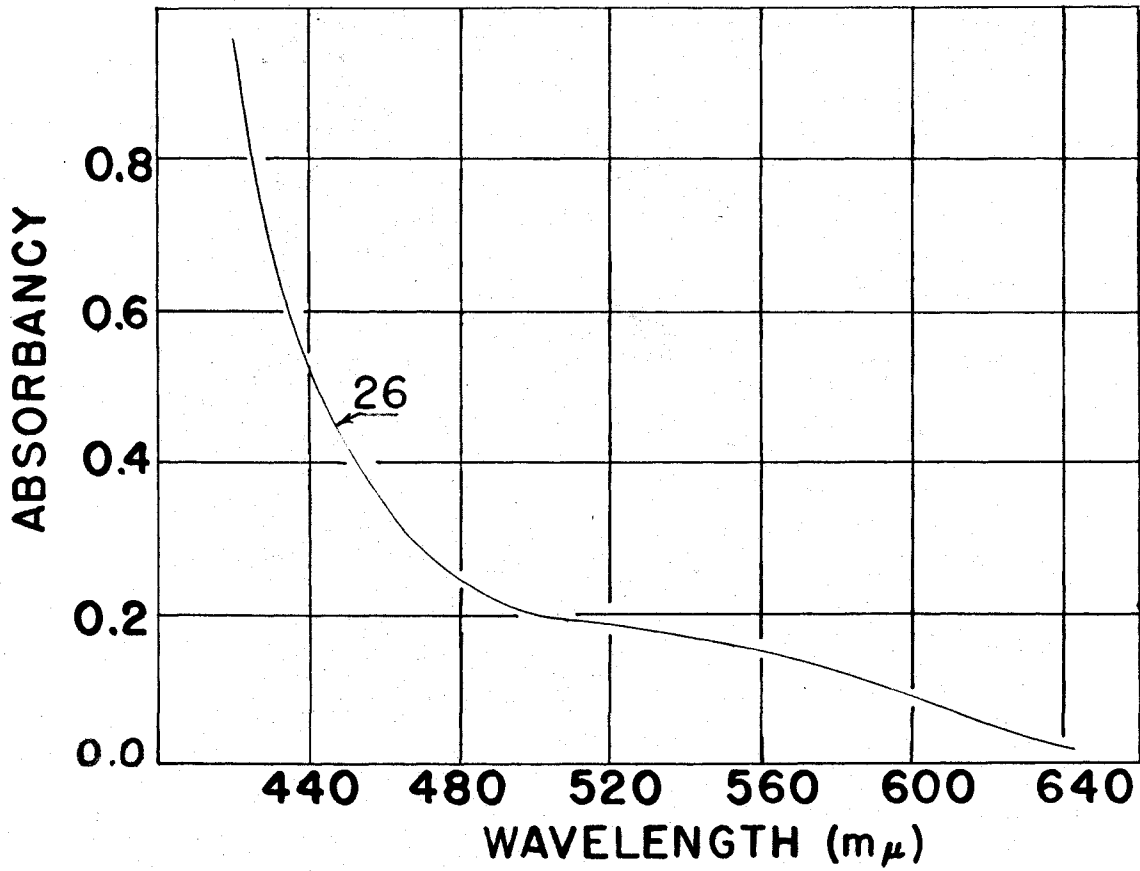
Figure 13. Absorption Characteristics of an Aqueous
Solution of Manganese(III), (IV) in 2 M
Perchloric Acid and 0.50$_0$ M Iodic Acid.

$$K_c = \frac{[Mn^{III}]^2}{[Mn^{II}][Mn^{IV}]} = \frac{(2x)^2}{(p-x)(m-x)}. \qquad (27)$$

However the titrating solution contained Mn^{III} as well as Mn^{IV}. If the ratio of manganese(III) to manganese(IV) was f, then the quantities became $(p-x)$, $(m-x)$, and $(2x+fm)$, and the equilibrium constant was

$$K_c = (2x+fm)^2/ (p-x)(m-x). \qquad (28)$$

This quantity was essentially constant for any titration in which the hydrogen ion and iodate ion concentrations, the temperature, the ionic strength, and consequently the activity coefficients of the species did not vary. It was possible that several species of each manganese oxidation state existed in the solutions, but the ratios between all activities and concentrations for the species of a given oxidation state would have been constant for equilibrium solutions with these same properties.

When equation 28 was solved for x, the following expression was obtained

$$x = \frac{-(4fm+pK_c+mK_c)}{8-2K_c}$$

$$\pm \frac{[K_c^2(p-m)^2 + K_c(8fmp+8fm^2+4f^2m^2+16pm)]^{\frac{1}{2}}}{8-2K_c}. \qquad (29)$$

Letting y be m/p, the expression was

$$x = \frac{-(4fpy + K_c p + K_c py)}{8 - 2K_c}$$

$$\pm \frac{[K_c^2 (p-py)^2 + K_c (fp^2 y + 8fp^2 y^2 + 4f^2 p^2 y^2 + 16yp^2)]^{\frac{1}{2}}}{8 - 2K_c} \quad (30)$$

and $(p - x) = [(8p - 2K_c p)/(8 - 2K_c)] - x$ (31)

or $(p - x) = \dfrac{8p - K_c p + 4fyp + K_c py - Y^{\frac{1}{2}}}{8 - 2K_c},$ (32)

where Y is the quantity in the radical in the equation for x.
In terms of the above symbols the Nernst equation,

$$E = E^o - (RT/nF) \ln a_{Mn^{+++}} / a_{Mn^{++}} ,$$

became

$$E = E^o - (RT/nF) \ln \frac{(2x + fm)}{(p - x)} \frac{\gamma_{III}}{\gamma_{II}} \quad (33)$$

if oxidation potentials were considered. When the Nernst
equation was written in terms of y and K_c only, the following
working form was obtained:

$$E = \text{constant} - \frac{RT}{nF} \quad (34)$$

$$\ln \frac{-2K_c \{1 + y + fy - [(1-y)^2 + (8fy + 8fy^2 + 4f^2 y^2 + 16y)/K_c]^{\frac{1}{2}}\}}{8 - K_c \{1 - y - 4fy/K_c + [(1-y)^2 + (8fy + 8fy^2 + 4f^2 y^2 + 16y)/K_c]^{\frac{1}{2}}\}} \cdot$$

The K_c' values from the experimental curves were used in
the above equation, and points for corresponding theoretical
plots were calculated. In most cases the experimental and
calculated curves were superimposable; a few small deviations
were observed especially in that portion of the curve imme-

diately preceding or following the greatest change in potential, and the deviations were of the magnitude of the expected experimental error. In order to obtain a better fit between the theoretical points and the experimental data, new curves were calculated using K_c' values slightly different than the values listed in Table 3. The equilibrium constant for the theoretical curve which most closely matched the experimental curve was taken as the best value for the constant; these values are listed as K_c values in Table 3 along with the points for the corresponding theoretical curves. The theoretical points are indicated in Figures 3 to 12 by the isolated circles.

In this treatment of the experimental data the K_c values obtained were constants only for the particular set of experimental conditions imposed during the titration. The variations in these concentration equilibrium constants with iodate ion and hydrogen ion concentrations, ionic strength, and temperature gave some information about the actual equilibrium involved. An exact theoretical calculation of activity coefficients could not be made for solutions of the concentrations used, namely, 0.25 M to over 2 M. However by studying the effects of the factors influencing the equilibrium, a concentration equilibrium constant was evaluated.

The effect of iodate and hydrogen ion was investigated separately in experiments sixteen to twenty-four inclusive.

Table 3

Calculated Potentials and Corresponding Equilibrium Constants

y values	Calculate Potentials for Experiment Number					
	1	2	3	4	5	6
0.2	-0.145	-0.136	-0.128	-0.138	-0.126	-0.134
0.4	-0.122	-0.112	-0.102	-0.113	-0.098	-0.111
0.6	-0.103	-0.092	-0.079	-0.092	-0.075	-0.092
0.8	-0.080	-0.067	-0.053	-0.067	-0.048	-0.069
0.9	-0.061	-0.046	-0.033	-0.047	-0.029	-0.050
1.0	0.000	0.000	0.000	0.000	0.000	0.000
1.1	0.058	0.044	0.030	0.044	0.026	0.047
1.2	0.074	0.060	0.048	0.061	0.042	0.063
1.4	0.090	0.077	0.064	0.078	0.060	0.078
1.6	0.099	0.087	0.074	0.088	0.070	0.087
1.8	0.105	0.094	0.083	0.095	0.078	0.092
2.0	0.110	0.099	0.087	0.100	0.083	0.097
2.4	0.117					0.103
3.0	0.124	0.114	0.103	0.115	0.100	0.110
4.0	0.131	0.122	0.112	0.123	0.109	0.116
5.0	0.136	0.126	0.117			0.120
K'_c	7.43×10^4	$1.5_4 \times 10^4$	$3.6_3 \times 10^3$	1.46×10^4	2.29×10^3	$3.4_5 \times 10^4$
ΔE (Average value for titrations, Table 2)	0.264	0.246	0.225	0.247	0.220	0.246
K_c (From a matched calculated curve)	7.44×10^4	$1.5_3 \times 10^4$	3.76×10^3	1.51×10^4	2.29×10^3	$3.3_9 \times 10^4$

Table 3

(Continued)

y values	Calculate Potentials for Experiment Number					
	7	8	9	10	11	12
0.2	-0.123	-0.112	-0.105	-0.160	-0.150	-0.155
0.4	-0.098	-0.085	-0.077	-0.136	-0.121	-0.130
0.6	-0.077	-0.064	-0.054	-0.117	-0.101	-0.110
0.8	-0.052	-0.039	-0.030	-0.094	-0.074	-0.085
0.9	-0.033	-0.021	-0.015	-0.075	-0.052	-0.064
1.0	0.000	0.000	0.000	0.000	0.000	0.000
1.1	0.031	0.019	0.014	0.072	0.040	0.061
1.2	0.046	0.032	0.024	0.088	0.067	0.078
1.4	0.062	0.048	0.039	0.103	0.084	0.094
1.6	0.072	0.058	0.048	0.112	0.094	0.104
1.8	0.078	0.065	0.055	0.118	0.101	0.110
2.0	0.083	0.070	0.060	0.122	0.106	0.115
2.4	0.088	0.077	0.068	0.128	0.116	0.121
3.0	0.096	0.084	0.076	0.134	0.126	0.128
4.0	0.103	0.091	0.083	0.141	0.128	0.135
5.0	0.108	0.096	0.088	0.144	0.132	0.139
K_c'	$5.8_2 \times 10^3$	1.46×10^3	$5.7_0 \times 10^2$	$3.1_5 \times 10^5$	2.26×10^4	8.06×10^4
ΔE (average value for titrations, Table 2)	0.221	0.199	0.183	0.298	0.277	0.288
K_c (from a matched calculated curve)	$5.8_9 \times 10^3$	$1.4_4 \times 10^3$	$5.6_9 \times 10^2$	$3.2_3 \times 10^5$	$2.2_4 \times 10^4$	$8.1_2 \times 10^4$

Table 3

(Continued)

y values	Calculate Potentials for Experiment Number					
	13	14	15	16	17	18
0.2	-0.146	-0.115	-0.101	-0.127	-0.116	-0.105
0.4	-0.117	-0.092	-0.077	-0.102	-0.091	-0.080
0.6	-0.094	-0.073	-0.056	-0.081	-0.070	-0.060
0.8	-0.065	-0.050	-0.033	-0.056	-0.046	-0.036
0.9	-0.043	-0.032	-0.018	-0.037	-0.028	-0.020
1.0	0.000	0.000	0.000	0.000	0.000	0.000
1.1	0.040	0.030	0.016	0.035	0.026	0.018
1.2	0.058	0.044	0.028	0.051	0.041	0.031
1.4	0.076	0.059	0.042	0.068	0.057	0.047
1.6	0.087	0.067	0.051	0.078	0.067	0.056
1.8	0.094	0.073	0.057	0.085	0.074	0.064
2.0	0.099	0.078	0.062	0.091	0.080	0.069
2.4	0.107	0.084	0.069	0.099	0.088	0.077
3.0	0.114	0.090	0.078	0.109	0.097	0.086
4.0	0.122	0.097	0.082	0.117	0.106	
5.0	0.127	0.101	0.086			
K_c'	$9.3_3 \times 10^3$	$6.5_9 \times 10^3$	$1.1_4 \times 10^3$	$5.5_1 \times 10^3$	$2.3_3 \times 10^3$	$9.8_4 \times 10^2$
ΔE (average value for titrations, Table 2)	0.266	0.207	0.179	0.220	0.198	0.176
K_c (from a matched calculated curve)	$9.3_3 \times 10^3$	$6.6_8 \times 10^3$	$1.1_4 \times 10^3$	$5.5_1 \times 10^3$	$2.3_3 \times 10^3$	$9.8_4 \times 10^2$

Table 3

(Continued)

y values	Calculate Potentials for Experiment Number						
	19	20	21	22	23	24	25
0.2	-0.091	-0.128	-0.118	-0.107	-0.096	-0.116	-0.128
0.4	-0.067	-0.103	-0.093	-0.082	-0.072	-0.091	-0.105
0.6	-0.047	-0.083	-0.073	-0.062	-0.051	-0.071	-0.087
0.8	-0.025	-0.058	-0.048	-0.038	-0.029	-0.046	-0.064
0.9	-0.013	-0.038	-0.030	-0.021	-0.015	-0.028	-0.045
1.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1.1	0.012	0.036	0.027	0.020	0.014	0.026	0.045
1.2	0.022	0.052	0.043	0.033	0.024	0.041	0.057
1.4	0.035	0.069	0.059	0.049	0.039	0.057	0.073
1.6	0.044	0.080	0.069	0.059	0.048	0.067	0.081
1.8	0.051	0.086	0.076	0.066	0.055		
2.0	0.056	0.091	0.082	0.071	0.060	0.079	0.092
2.4	0.064	0.100	0.090	0.080	0.069	0.087	0.098
3.0	0.073	0.110	0.100	0.089	0.078	0.095	0.104
4.0	0.084				0.088	0.103	0.111
5.0	0.093						
k_c'	$3.9_8 \times 10^2$	$6.9_7 \times 10^3$	$3.1_8 \times 10^3$	$1.3_4 \times 10^3$	$5.6_9 \times 10^2$	$2.7_2 \times 10^3$	$2.0_0 \times 10^4$
ΔE (average value for titrations, Table 2)	0.153	0.226	0.206	0.184	0.162	0.202	0.233
k_c (from a matched calculated curve)	$3.9_0 \times 10^2$	$6.9_7 \times 10^3$	$3.1_7 \times 10^3$	$1.3_4 \times 10^3$	$5.6_7 \times 10^2$	$2.7_2 \times 10^3$	$2.0_7 \times 10^4$

In this series the ionic strength was maintained effectively constant by using lithium perchlorate and perchloric acid mixtures with a total concentration of 2 M; in no case was the acid strength less than 1 M. Various concentrations of iodic acid from 0.5 to 1.0 M were used, but due to its small dissociation constant, the resulting contribution to the ionic strength or acidity was small in the presence of the perchloric acid. This dissociation constant, as given by Fuoss and Kraus (58), is 0.168 at 25°C; therefore the hydrogen ion concentration remained approximately equal to the perchloric acid strength, and the iodate ion existed in low concentrations. In experiments 16 to 19 inclusive the solutions used were 2 M in perchloric acid and consequently approximately 2 M in hydrogen ion. In experiments 20 through 23 the hydrogen ion concentration was maintained effectively at 1 M with perchloric acid, and the ionic strength was maintained at 2 moles per liter by making the solutions 1 M in lithium perchlorate also. Due to the lower acidity in this set of experiments, the iodic acid dissociated to a greater extent and larger variations occurred in the hydrogen ion concentration. These data are given in Table 4.

To determine the iodate dependence the accepted method would have been to plot the logarithm of the equilibrium constant against the logarithm of the iodate ion concentration. However, due to the unknown effects of the high ionic

strength, exact calculations of iodate concentrations were not possible. Approximate concentrations were calculated assuming the ratio of the activity coefficients was a constant for solutions of the same ionic strength and temperature and was equal to unity. Sample computations using data from titration 16 show the method employed to obtain these values.

The dissociation constant of iodic acid at $23.4°C$ was calculated to be 0.169 using the value of 0.168 at $25°$ reported by Fuoss and Kraus (58) and the ΔH of -2900 calories per mole given by Abel and co-workers (60). K_a was written in the form:

$$K_a = 0.169 = \frac{[H^+][IO_3^-]}{[HIO_3]} \frac{\gamma_{H^+} \gamma_{IO_3^-}}{\gamma_{HIO_3}} \tag{35}$$

or

$$[IO_3^-] = \frac{K_a [HIO_3]}{[H^+]} \frac{\gamma_{HIO_3}}{\gamma_{H^+} \gamma_{IO_3^-}} = \frac{0.169 (1 - [IO_3^-])}{2 + [IO_3^-]} \tag{36}$$

and $[IO_3^-] = 0.074_5$ for 1 M HIO_3 and 2 M $HClO_4$. These data are listed in Table 4.

Plots of the logarithm of K_c against log $[IO_3^-]$ were made, as shown in Figure 14, using the approximate or estimated iodate ion concentrations. Straight lines were produced which had slopes of 3.92 for 2 M perchloric acid solutions, curve 27, and 3.91 for 1 M perchloric acid solutions, curve 28. A fourth power dependence on iodate concentration

was indicated. In order to determine the effect of possible activity factors on the estimated iodate ion concentrations, the calculations were repeated for the 2 M perchloric acid solutions using 0.2, 1.5, and 5 for the activity coefficient factor. In addition similar calculations were made for the 1 M perchloric acid solutions using the factor of 1.5. The logarithm of the values obtained, as listed in Table 4, were plotted against the log K_c, and straight lines were obtained of slope 4.18 for an activity factor of 0.2, curve 29, Figure 15, 3.97 for an activity factor of 1.5, curve 30, Figure 15, and 4.08 for an activity factor of 5, curve 32, Figure 15, in 2 M perchloric acid. The slope of line 31, Figure 15, for 1 M perchloric acid was 3.96. Since these large changes in the values given to the activity coefficient factor did not affect the slopes of the lines materially, it was assumed that the calculated values for the iodate ion concentration were approximately proportional to the true concentrations, and a fourth power dependence on iodate ion concentration was assumed correct.

With the above value for the iodate dependence, it was possible to use the data from curves 16 through 23 and from curve 24 for a titration in 1.5 M perchloric acid to determine the hydrogen ion dependence. The iodate dependence was accounted for by dividing the equilibrium constant, K_c, by the fourth power of the estimated iodate concentrations, and

Table 4

Calculated Ionic Concentrations for Titrations in Perchloric Acid Solutions

| Titration Number	$M^a_{HIO_3}$	Assumed Activity Coefficient Factor	Estimated $M[IO_3^-]$	$M[H^+]$	log $[IO_3^-]$	log $[H^+]$	log K_c
16	1.00	1.0	0.074_5	2.074_5	-1.128	0.317	3.741
17	0.80	1.0	0.060_3	2.060_3	-1.220	0.314	3.367
18	0.64	1.0	0.048_5	2.048_5	-1.319	0.312	2.993
19	0.50	1.0	0.038_0	2.038_0	-1.420	0.309	2.590
20	1.00	1.0	0.129	1.129	-0.889	0.053	3.843
21	0.80	1.0	0.105	1.105	-0.979	0.043	3.502
22	0.64	1.0	0.085	1.085	-1.071	0.036	3.128
23	0.50	1.0	0.068	1.068	-1.167	0.029	2.754
24	0.80	1.0	0.077	1.577	-1.114	0.198	3.435
16	1.00	0.2	0.016	2.016	-1.796	0.305	3.741
17	0.80	0.2	0.013	2.013	-1.886	0.304	3.367
18	0.64	0.2	0.010_5	2.010_5	-1.979	0.303	2.993
19	0.50	0.2	0.008_5	2.008_5	-2.071	0.303	2.590
16	1.00	5.0	0.270_5	2.270_5	-0.569	0.356	3.741
17	0.80	5.0	0.219	2.219	-0.660	0.341	3.367
18	0.64	5.0	0.178	2.178	-0.750	0.338	2.993
19	0.50	5.0	0.141	2.141	-0.851	0.331	2.590
16	1.00	1.5	0.106_5	2.106_5	-0.972	0.324	3.741
17	0.80	1.5	0.086_0	2.086_0	-1.065	0.320	3.367
18	0.64	1.5	0.069_5	2.069_5	-1.158	0.316	2.993
19	0.50	1.5	0.054_5	2.054_5	-1.263	0.313	2.590
20	1.00	1.5	0.176_5	1.176_5	-0.753	0.071	3.843
21	0.80	1.5	0.144_5	1.144_5	-0.845	0.059	3.502
22	0.64	1.5	0.117_5	1.117_5	-0.930	0.048	3.128
23	0.50	1.5	0.093_5	1.093_5	-1.029	0.039	2.745
25	1.00	1.0	0.110_5	2.110_5	-0.956	0.325	4.316

^{a}M refers to molarity.
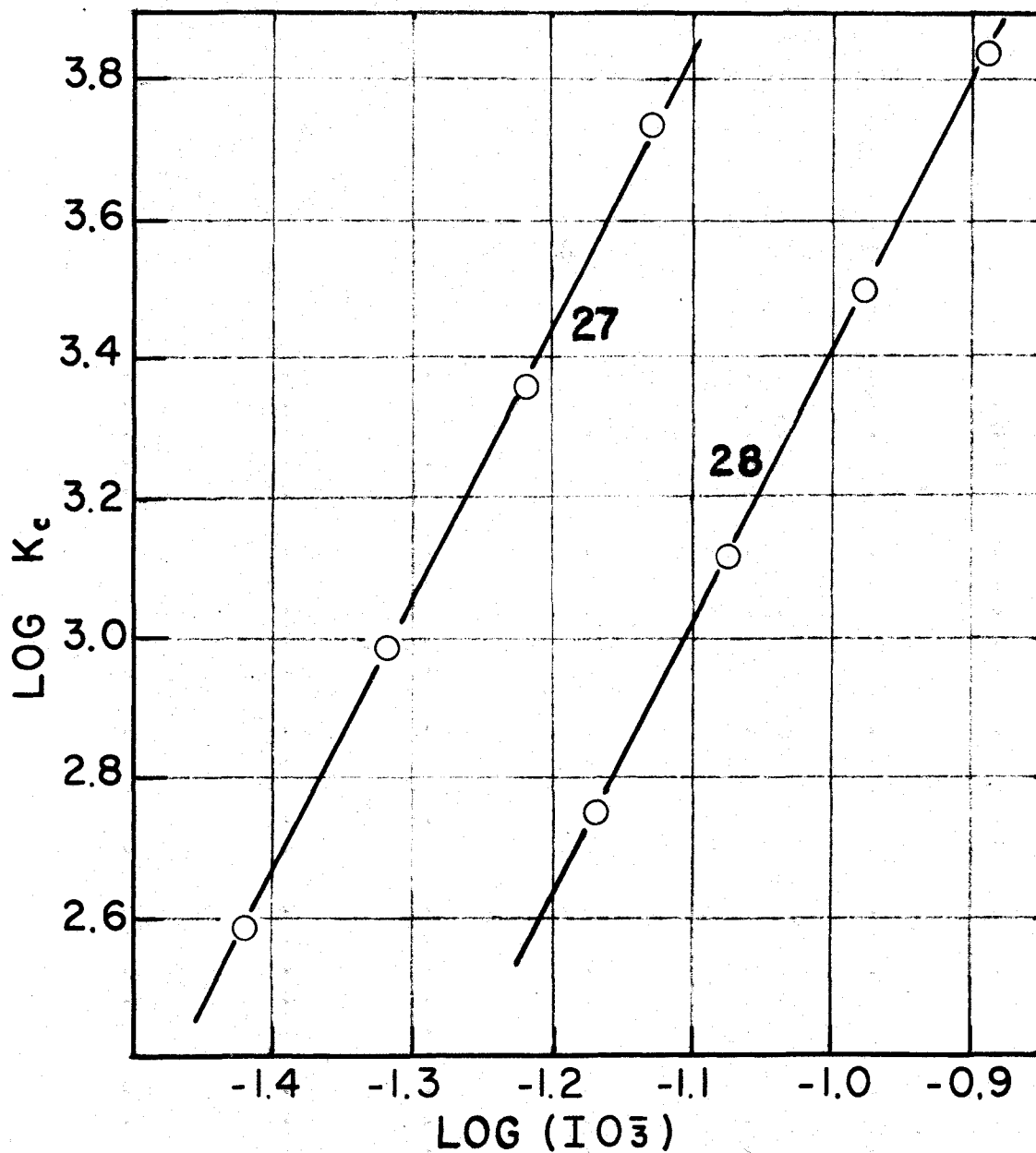
Figure 14. The Variation of the Equilibrium Constant, K_c, With Iodate Ion Concentration Using an Activity Coefficient Factor of One. Curves: 27, 2 M Perchloric Acid; 28, 1 M Perchloric Acid.
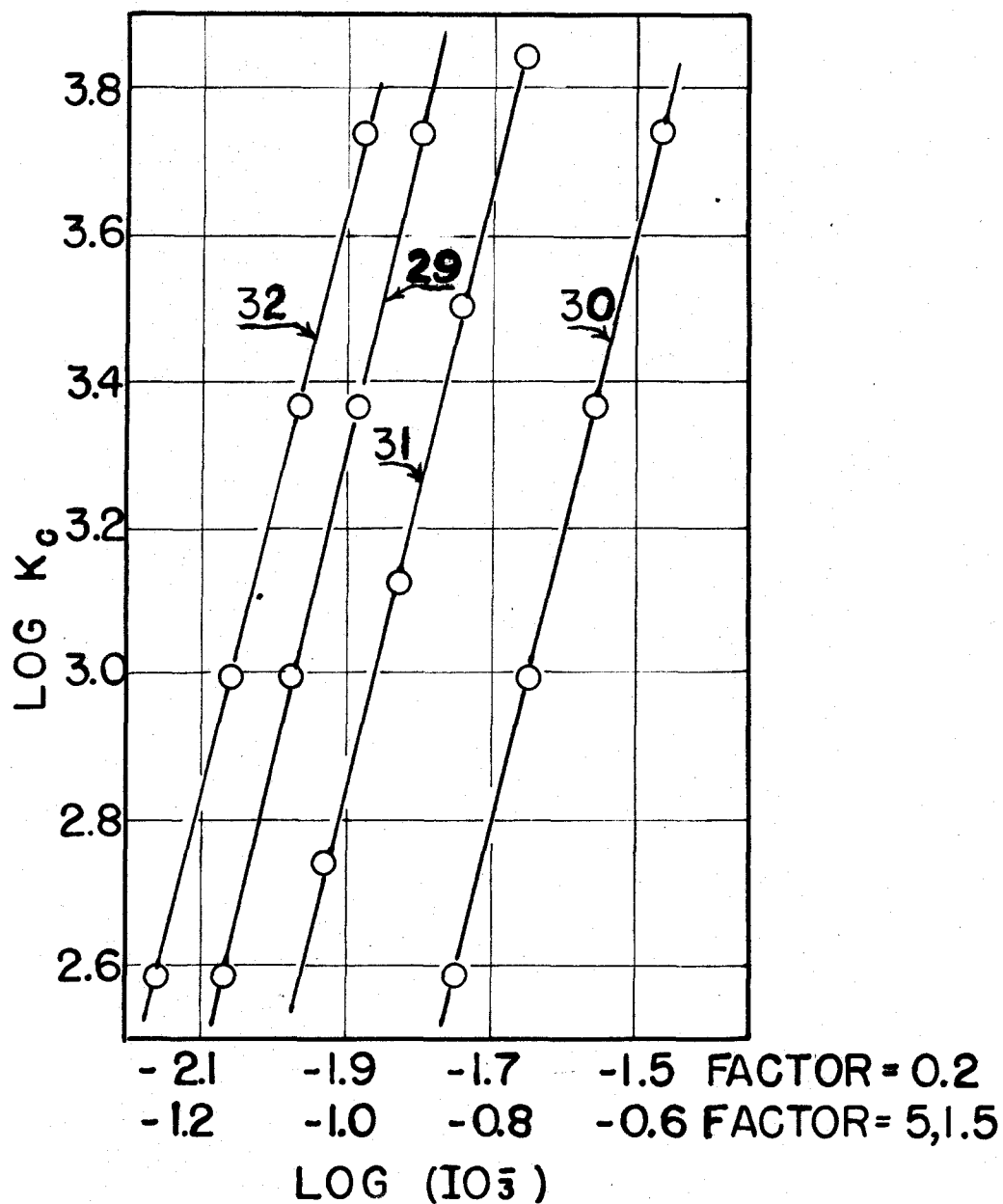
Figure 15. The Variation of the Equilibrium Constant, K_c, With Iodate Ion Concentration Using Activity Coefficient Factors of 0.2, 1.5, and 5.0. Curves: 29, 0.2 Activity Coefficient Factor, 2 M Perchloric Acid; 30, 1.5 Activity Coefficient Factor, 2 M Perchloric Acid; 31, 1.5 Activity Coefficient Factor, 1 M Perchloric Acid; 32, 5 Activity Coefficient Factor, 2 M Perchloric Acid.

the logarithm of the hydrogen ion concentration was plotted
against this dividend as shown in Figure 16. Since only the
slope of the curve was required and not the intercept, the
proportionality constant showing the relationship between the
actual and the calculated iodate concentrations was not con-
sidered. A spread in the points occurred due to the slight
variation in the hydrogen ion concentrations with the various
iodic acid strengths; these data are listed in Table 4. The
plot of the data in which the activity coefficient factor was
set equal to unity produced a straight line with a slope of
3.04, curve 33, Figure 17. When the concentrations were cal-
culated using a factor of 1.5, a slope of 2.92, curve 34, was
obtained, and a third order dependence on the hydrogen ion
concentration was indicated.

With the determination of the dependence of the equilib-
rium reaction on the iodate ion and hydrogen ion concentra-
tions, it was possible to describe the equilibrium more com-
pletely, and to write the overall reaction,

$$Mn^{IV} + Mn^{II} + 4\ IO_3^- + 3\ H^+ \rightleftharpoons 2\ Mn^{III}. \quad (37)$$

At this point sufficient information concerning the equilib-
rium had been obtained to speculate upon the nature of the
manganese species involved. It was possible that more than
one species of each manganese oxidation state existed in
equilibrium with the form active in the manganese(II), (III),
(IV) equilibrium. However, if such were the case no support-

ing experimental evidence for it was obtained. Since the colorimetric analyses checked the potentiometric endpoints in all cases tested even with widely different hydrogen and iodate concentrations, either the formation of several species did not alter the absorption characteristics of the solutions or a single species dominated each oxidation state. In addition, if more than one species existed for each oxidation state, the power of the dependence of K_c on iodate and hydrogen ion concentrations would not necessarily be constant and integral but could vary with the relative amounts of each complex present. In order to test the constancy completely a wider range of manganese concentrations than was used in these experiments would be required. However, integral values which were constant for the manganese concentrations used were obtained.

From the electrolysis experiments it was known qualitatively that the manganese(III) and manganese(IV) species were negatively charged. If any positive complexes existed in the solutions tested, they were present in such low concentrations that their movement toward the negative electrode was not evident.

From the information gained during the preparation of the manganese solutions, it was known that iodate was necessary for the formation of the manganese(III) and manganese(IV) solutions; it was reasonable to assume that iodate ion was contained in the complexes of each oxidation state.
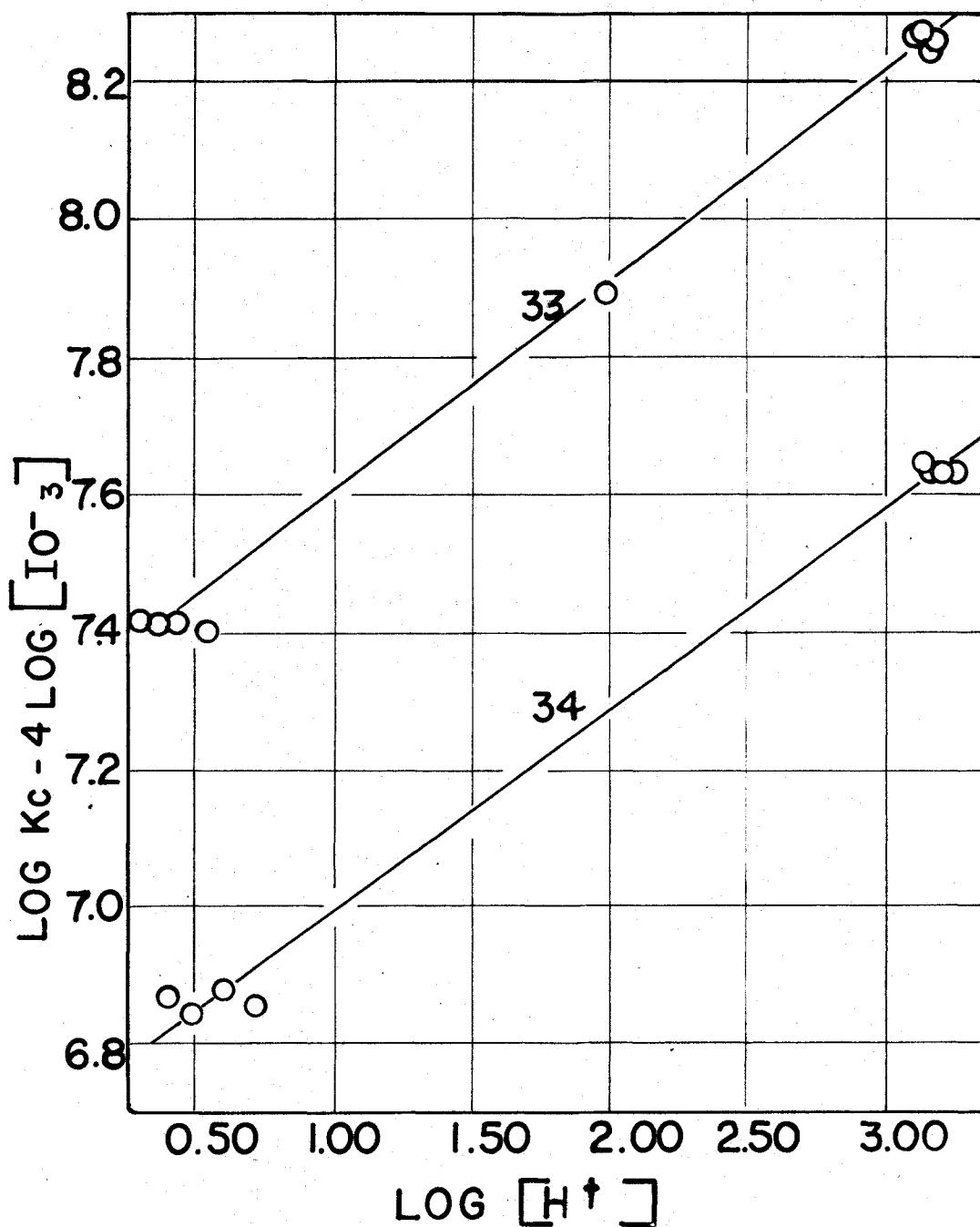
Figure 16. The Variation of the Concentration Equilibrium
Constant, K_c, With Hydrogen Ion Concentration.
Curves: 33, 1.0 Activity Coefficient Factor;
34, 1.5 Activity Coefficient Factor.

However work reported by Hayes and Martin (59) indicated that manganese(II) iodate was completely dissociated in aqueous solution; therefore this species probably existed as the single divalent ion. From a consideration of reaction 37 it was evident that two molecules of the trivalent complex contained four more iodate ions than the manganese(IV) species. In addition the dependence of the reaction on hydrogen ion indicated a higher degree of hydrolysis in the reactants than in the products, but the possibility of a hydroxylated manganese(III) iodate was not excluded. Several authors (4, 5, 15, 21, 24) have postulated manganese(IV) species which contained such ions as oxide and hydroxide, but no discussion of trivalent manganese complexes of this type was found.

In the postulation of possible complex species the small size of the manganese atom precluded consideration of structures which required a coordination number greater than six. Many complexes have been reported for the first transition series, and the common value for the coordination number is six; in general octahedral structures are formed. It was not the intention here to discuss the structure of the manganese complexes formed in the iodate solutions but only to try to formulate species which appeared reasonable when the above evidence was considered.

A general formula for the manganese(III) complex which

would satisfy the experimentally determined restrictions was written as $Mn^{III}(IO_3)_n(OH)_m$ where the sum of m and n was greater than three. The manganese(IV) species was postulated to be $Mn^{IV}(O)_p(OH)_q(IO_3)_r$ where the sum, $(2p + q + r)$, was greater than four. The equilibrium reaction was rewritten using these general formulas as follows:

$$Mn^{IV}(O)_p(OH)_q(IO_3)_r^{-v} + Mn^{++} + 3 H^+ + 4 IO_3^-$$

$$\rightleftharpoons 2 Mn^{III}(IO_3)_n(OH)_m^{-w} + s H_2O . \quad (38)$$
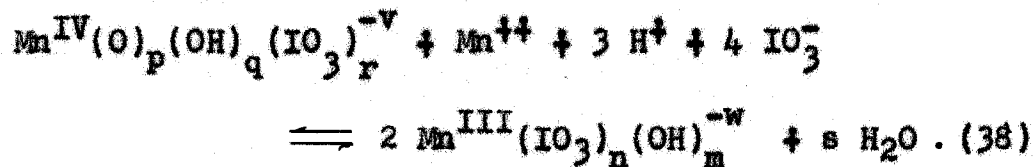
It was seen from this general equation that n was equal to $(4 + r)/2$. If a coordination number of six was assumed for manganese, further restrictions were imposed upon the possible values for the subscripts. Since the magnitude of the charges, v and w, were not known, it was impossible to determine the formulas more definitely until ionic strength effects on the reaction had been considered.

The effect of ionic strength, μ, was not simply resolved. Since both hydrogen and iodate ions were necessary to obtain a measurable equilibrium constant, systems in which the effect of ionic strength was studied had to contain iodic acid. The ionization of the iodic acid was dependent upon μ also, and the hydrogen and iodate ion concentrations varied when the total ionic molarities were changed. Consequently no simple system was available in which the effect of ionic strength could be isolated and studied.

One approach to the problem which yielded qualitative results utilized data from experiments one through fifteen. From the K_c values in these experiments, the effect of temperature and iodic acid concentration on the equilibrium was obtained. Since iodic acid was the main solute in the solutions used in these titrations, the ionic strength varied with the iodic acid strength and degree of dissociation which was temperature dependent. A heat of dissociation of -2900 calories per mole was reported for this acid by Abel and co-workers (60).

A qualitative examination of these data showed that the equilibrium constant varied inversely as the temperature and directly as the iodic acid concentration. The effect of both of these variables on the equilibrium was large. K_c varied from 3.2_3X10^5 for 1.78 M iodic acid to 6.6_8X10^3 for 0.25 M iodic acid solutions at $0^{\circ}C$. The ratio of the concentrations was 7.12 in this case whereas the ratio of the equilibrium constants was 47.3. When the temperature was increased from $0^{\circ}C$ to $57.2^{\circ}C$, the K_c values decreased from 7.4_4X10^4 to 2.2_9X10^3. These variations with temperature and iodic acid concentrations were more easily seen from the customary plots of log K_c against $1/T$ as shown in Figure 17. Straight lines were produced for each iodic acid concentration over the temperature range investigated. Curves 35, 36, 37, and 38, Figure 17, represented data for 1.782 M, 0.990 M, 0.497 M, and
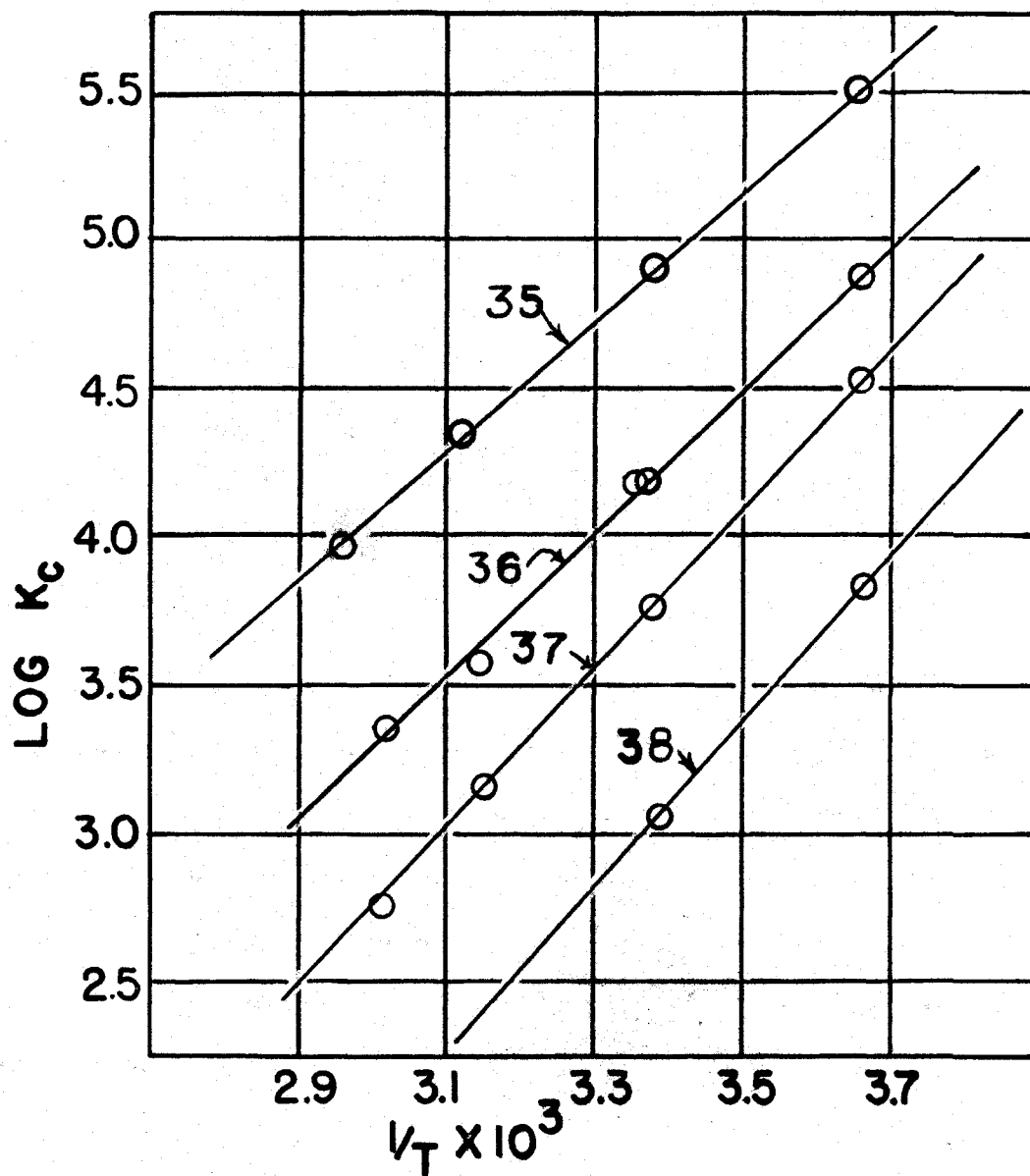
Figure 17. The Variation of the Equilibrium Constant, K_c, With Temperature at Four Iodic Acid Concentrations. Curves: 35, 1.78_2 M HIO_3; 36, 0.990 M HIO_3; 37, 0.497 M HIO_3; 38, 0.249 M HIO_3.

0.249 M iodic acid solutions respectively.

Abel, Redlich, and Hersch (60) have reported values obtained from freezing point data for the activity coefficients of aqueous solutions from 0.001 to over 10 molal in iodic acid. In their work the dissociation constant for iodic acid was written as

$$K = \alpha^2 \beta^2 m/(1 - \alpha). \qquad (39)$$

where α was the degree of dissociation and β^2 was the activity coefficient function. The product, $(\alpha\beta)$ was given as a function of the molality; a plot of their data is given in Figure 18. The molar concentrations used in the present experimental work were converted to molalities using the solution densities for iodic acid reported by Groschuff (61) and Kraus and Parker (62). Values for $(\alpha\beta)$ corresponding to the experimental molalities were read from the curve in Figure 18. The dissociation constant for iodic acid of 0.262 at 0°C, as given by Abel and co-workers, was found to be in accord with the constant of 0.168 at 25°C and a ΔH of -2900 calories. The known quantities were substituted into equation 39 and values for the degree of dissociation were calculated for each molality used. The iodate ion concentration which was equal to the ionic strength in this case was calculated from the product of the molality and the degree of dissociation. Assuming β was independent of small temperature changes, the iodate ion concentrations were calculated at
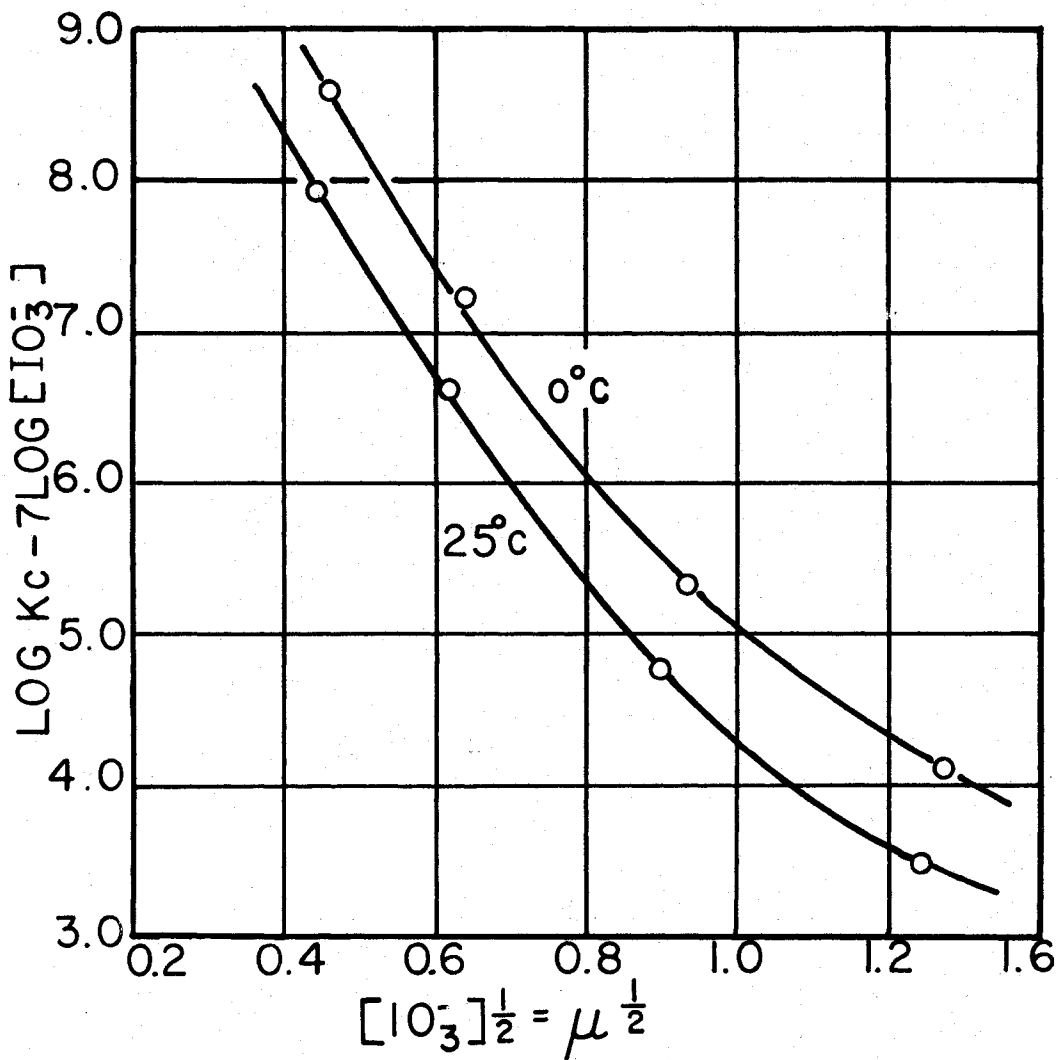
Figure 18. The Variation of the Equilibrium Constant With the Square Root of the Ionic Strength at 0°C and 25°C.

$25^\circ C$ also. The ionic molalities were converted back to molarities by multiplying each value by the (molarity/molality) ratio at the appropriate temperature for the solution.

With these actual concentrations it was possible to plot the ($\log K_c - 7\log [IO_3^-]$) against the square root of the ionic strength as shown in Figure 19 for the two temperatures. The meaning of the quantities plotted was more evident from a consideration of the equilibrium constant

$$K = \frac{[Mn^{III}]^2}{[Mn^{II}][Mn^{IV}][H^+]^3[IO_3^-]^4} \cdot \frac{\gamma_{Mn^{III}}}{\gamma_{Mn^{II}}\gamma_{Mn^{IV}}\beta_H + \gamma_{IO_3^-}^4} \quad (40)$$

for the overall reaction. The first term in the above expression consisted of the experimentally determined constant, K_c, and the hydrogen and iodate ion concentrations which were calculated. When the expression for K was rewritten in logarithmic form with the known quantities substituted into the equation, it became:

$$\log K = (\log K_c - 7 \log[IO_3^-]) + \log \Gamma \quad (41)$$

or

$$(\log K_c - 7 \log[IO_3^-]) = \log K/\Gamma \quad (42)$$

where Γ indicates the activity coefficient factor. It was evident from the above treatment that the curves in Figure 19 were equivalent to a plot of the logarithm of the activity coefficient factor versus the square root of the ionic strength. The general shape of the present experimental
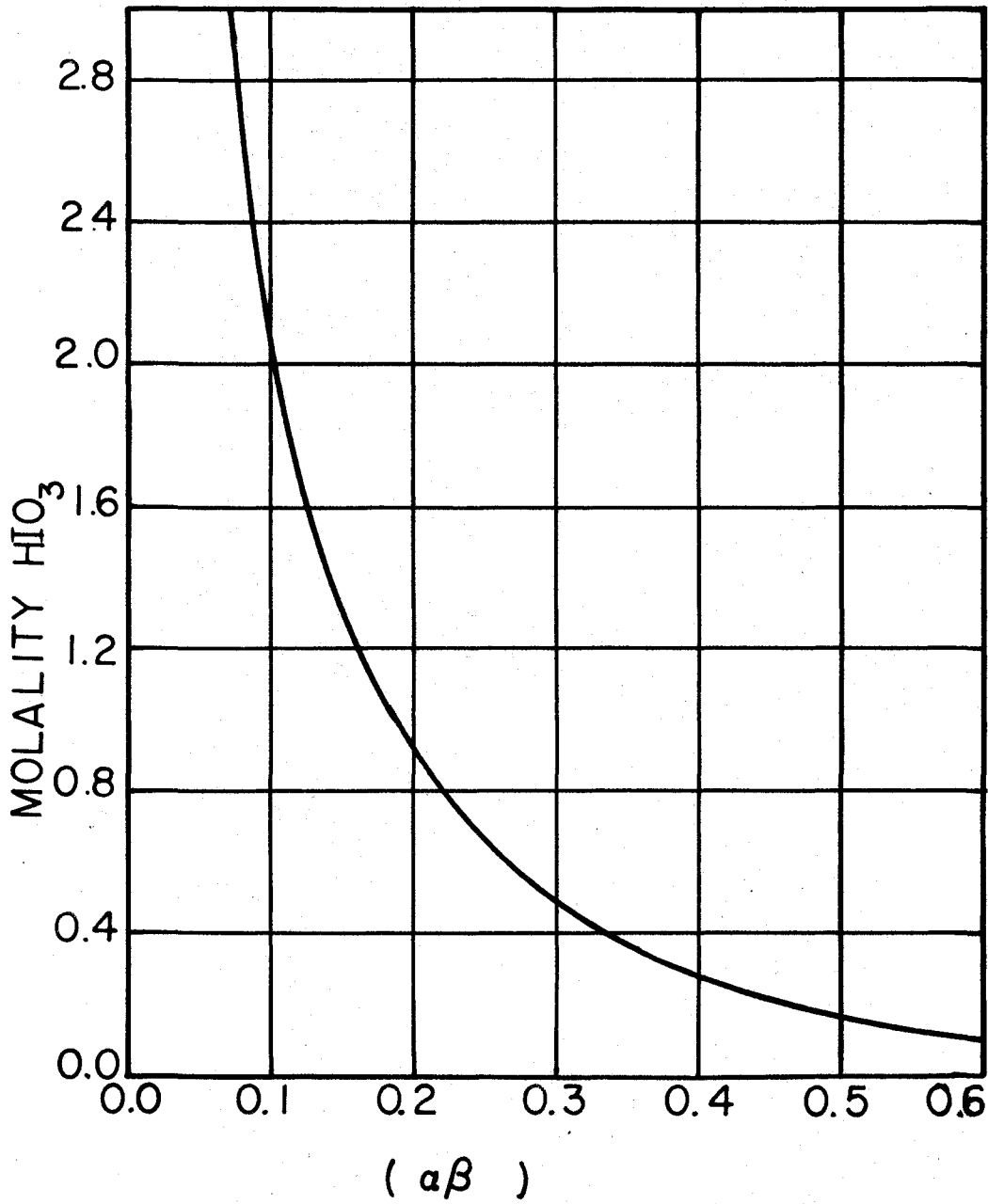
Figure 19. Relationship Between the Molality and the Product
of the Activity Coefficient and the Degree of
Dissociation for Iodic Acid at $0^{\circ}C$.

curves, when compared to similar curves for other electrolytes, showed that a normal change in activity coefficient with ionic strength existed.

Schumb and Sweetser (63) have used a treatment somewhat similar to the above to estimate equilibrium constants for solutions of ionic strength varying from 0.1 to 1.4. In their study of the reaction

$$Ag(s) + Fe^{+++} \rightleftharpoons Ag^+ + Fe^{++} , \tag{43}$$

they determined the concentrations of the ions at equilibrium. By utilizing an extended form of the Debye-Hückel equation,

$$\log \gamma_i = -A \, z_i^2 \, (\mu)^{\frac{1}{2}} + C_i \mu, \tag{44}$$

they were able to write the expression for their equilibrium constant in the following logarithmic form:

$$\log K = \log K_c^* - A \sum z_i^2 \, (\mu)^{\frac{1}{2}} + C \mu \tag{45}$$

where A was equal to 0.509 for aqueous solutions at 25°C, $\sum z_i^2$ was four in this case, C was a composite constant made up of the various C_i's, and K_c^* was the concentration equilibrium constant. Using a similar treatment for the present work, the following expression was obtained by combining equation 41 and 44:

$$\log K = (\log K_c - 7 \log [IO_3^-]) - A \sum z_i^2 \, (\mu)^{\frac{1}{2}} + C \mu. \tag{46}$$

By rearranging the above equation, it was seen that

$$\log K_c - 7 \log [IO_3^-] - A \sum z_i^2 \, (\mu)^{\frac{1}{2}} = \log K - C \mu \tag{47}$$

and that a plot of the left hand side of the expression, which was designated as P for convenience, against the ionic strength should be a straight line. With an extrapolation to μ equal to zero the intercept should give the value of log K. When Schumb and Sweetser used this method on their experimental data, they found that although the plots were not exactly linear this procedure provided a convenient method for estimating K.

In the present work, however, the structures and charges of the various species involved in the equilibrium were unknown except for the general formulas previously discussed.

It was known qualitatively that the manganese(III) and manganese(IV) species were negatively charged, a positive charge of two was assigned to the manganese(II) ion since it was considered a simple cation, and the iodate and hydrogen ions were assigned their normal negative and positive unit charges respectively. However values for the manganese(III) and manganese(IV) species could not be given, and the computation of $\sum z_i^2$ in equation 47 was not possible. Consequently a series of values of P were calculated in which $\sum z_i^2$ was assumed to be 0 to 30. Plots of P against μ were made as shown in Figure 20 for 0°C. The curve obtained by Schumb and Sweetser had a positive slope throughout. It was seen from the series of curves obtained that values of $\sum z_i^2$ of 12 and below produced curves with an initial negative slope and
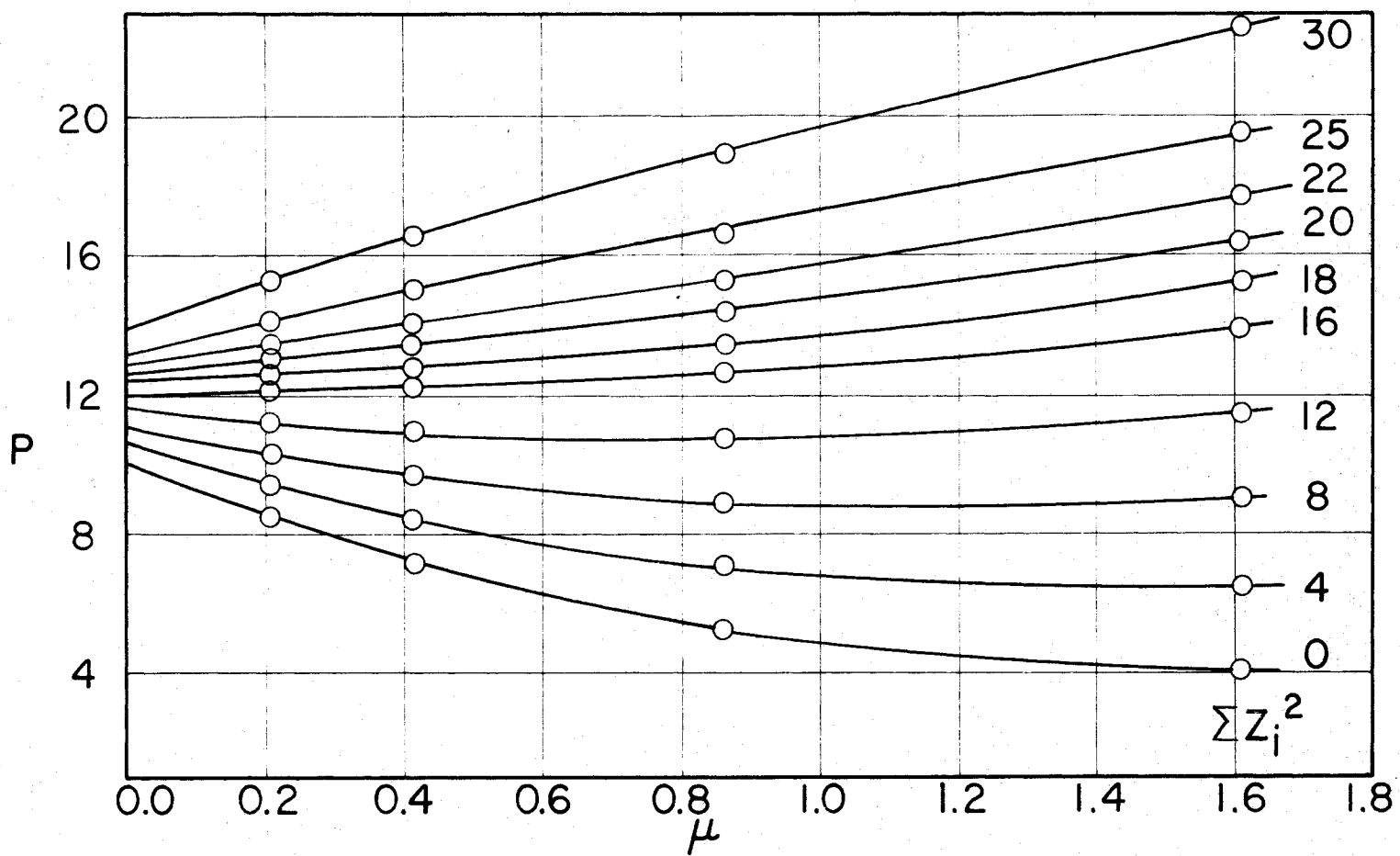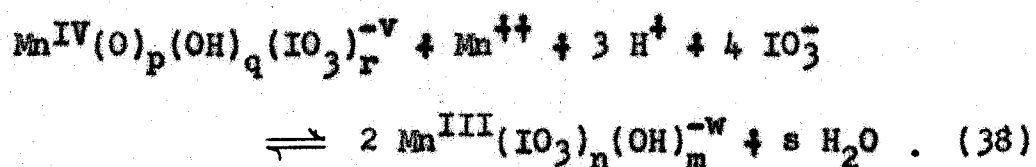
Figure 20. Variation of P With Ionic Strength for Various $\sum z_i^2$ Values at 0°C.

a minimum. In addition the plots more closely approximated straight lines as the $\sum z_i^2$ values increased to 22. Above 22, the curvature of the curves was negative. Actually values of 16 to 24 for $\sum z_i^2$ could be assumed to be appropriate if these plots were the only criterion. With this information concerning the overall charge for all of the species, the various possible combinations of the subscripts which included iodate in both the manganese(III) and manganese(IV) species and had a coordination number less than seven were tried in equation 38. The corresponding $\sum z_i^2$ values were calculated as shown in Table 5.

$$Mn^{IV}(O)_p(OH)_q(IO_3)_r^{-V} + Mn^{++} + 3\ H^+ + 4\ IO_3^-$$

$$\rightleftharpoons 2\ Mn^{III}(IO_3)_n(OH)_m^{-W} + s\ H_2O\ .\quad (38)$$

In most cases the combinations of subscripts tested gave incorrect hydrogen ion dependences; only four sets seemed possible. The three combinations which gave $\sum z_i^2$'s of 18 were selected as the most probable due to consideration of the plots of P against μ discussed previously. In two of these cases however, it was necessary to postulate a hydrolyzed manganese(III) species. It seems unlikely that the manganese(III) complex was hydrolyzed in the strongly acid solutions used. In the case of the oxalate system, Duke (64) reported evidence that hydroxylated trivalent manganese complexes did not exist. Therefore the combination of subscripts with m for the hydroxides in the manganese(III) complex

Table 5

Calculated $\sum z_i^2$ Values for Various Possible Manganese Complexes in the Equilibrium

p	q	r	v	n	m	w	z_i^2	s	
4	0	2	6	3	2	2	39		incorrect H$^+$ dependence
4	0	2	6	3	1	1	45		incorrect H$^+$ dependence
3	1	2	5	3	2	2	28	0	
3	0	2	4	3	1	1	25		incorrect H$^+$ dependence
2	2	2	4	3	2	2	19		incorrect H$^+$ dependence
2	2	2	4	3	1	1	25		incorrect H$^+$ dependence
2	1	2	3	3	1	1	18	1	
2	0	2	2	3	1	1	13		incorrect H$^+$ dependence
1	3	2	3	3	2	2	11		incorrect H$^+$ dependence
1	3	2	3	3	1	1	18	2	
1	2	2	2	3	1	1	13		incorrect H$^+$ dependence
1	1	2	1	3	1	1	10		incorrect H$^+$ dependence
0	4	2	2	3	2	2	7		incorrect H$^+$ dependence
0	4	2	2	3	1	1	13		incorrect H$^+$ dependence
0	3	2	1	3	1	1	10		incorrect H$^+$ dependence
2	0	4	4	4	1	2	19		incorrect H$^+$ dependence
2	0	4	4	4	0	1	25		incorrect H$^+$ dependence
1	1	4	3	4	1	2	12		incorrect H$^+$ dependence
1	1	4	3	4	0	1	18	2	
0	2	4	2	4	1	2	7		incorrect H$^+$ dependence
0	2	4	2	4	0	1	13		incorrect H$^+$ dependence
1	0	4	2	4	0	1	13		incorrect H$^+$ dependence
0	1	4	1	4	0	1	10		incorrect H$^+$ dependence
0	0	6	2	5	0	2	7		incorrect H$^+$ dependence

equal to zero was assumed to be the most likely for the present system. In such a case the only possibility was the reaction:

$$Mn^{IV}O(OH)(IO_3)_4^{---} + 3 H^+ + 4 IO_3^- + Mn^{++}$$
$$\rightleftharpoons 2 Mn(IO_3)_4^- + 2 H_2O . \qquad (48)$$
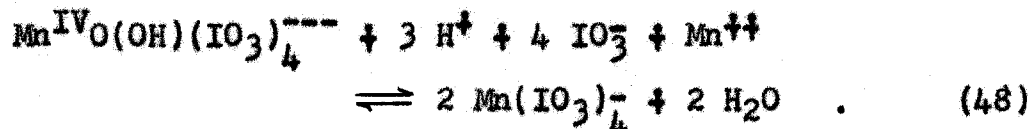
The possibilities of a higher coordination number for manganese, a hydrolyzed manganese(III) species, and a manganese(II) complex prevented making a definite statement of the actual reaction. However equation 48 is proposed as representing the most likely possibility.

Using data from experiments one through fifteen and a Σz_i^2 of 18, a similar plot of P against μ was made for 25°C. The curves for Σz_i^2 equal to 18 for 25°C and 0°C are shown in Figure 21. The intercepts for these curves were 12.4_0 for 0°C and 11.6_8 for 25°C which indicated the equilibrium constants for equation 48 were 2.5×10^{12} and 4.8×10^{11} respectively. Due to the uncertainty involved in the selection of the correct Σz_i^2 value and in the many assumptions, these values were recognized as a crude approximation at best for the thermodynamic equilibrium constant. It might be noted that in the reaction studied by Schumb and Sweetser a constant of 0.53 was estimated using the above procedure whereas the accepted value from other types of experiments was about 0.35.

From these approximate values for K a ΔH^0 of -11 kcal./

mole degree and a free energy change of $-15._5$ kcal. at 0°C were calculated.

The approximate concentration equilibrium constant for reaction 48 was calculated from the data for titrations 16 through 24 using the estimated concentrations for hydrogen and iodate ions. These titrations were all made at a constant ionic strength of two. An average value of -7.305 ± 0.021 for the pK or of 2.18×10^7 for the constant was obtained.

By adding the reaction for the dissociation of iodic acid to equation 48, the equilibrium reaction could be written

$$Mn^{++} + MnO(OH)(IO_3)_4^{---} + 4\ HIO_3$$
$$\rightleftharpoons 2\ Mn(IO_3)_4^- + H^+ + 2\ H_2O \qquad (49)$$
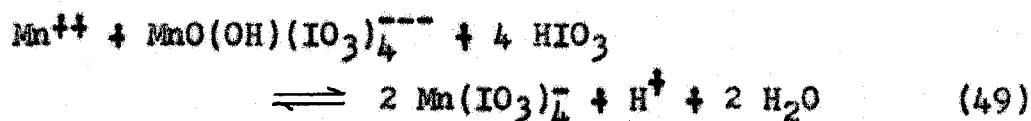
for which

$$_1K_c = \frac{[Mn(IO_3)_4^-]^2[H^+][H_2O]^2}{[Mn^{++}][MnO(OH)(IO_3)_4^{-3}][HIO_3]^4} . \qquad (50)$$

By this conversion to the form of equation 50, the use of estimated iodate ion concentrations was no longer necessary except as a correction factor in the hydrogen ion and iodic acid concentrations. The perchloric acid repressed the dissociation of the iodic acid and controlled the hydrogen ion concentration. It was possible therefore to calculate $_1K_c$ in 2 M perchloric acid solutions without introducing all of the error involved in the estimated iodate ion concentrations. Calculations of this constant were made for experiment 16 at 23.4°C and experiment 25 at 0°C, and values of

1.56X10^4 and of 7.00X10^4 respectively were obtained. From these values an approximate ΔH^o, which might be considered a temperature coefficient for the reaction, of -10 kcal./mole degree was calculated.

To compare the ΔH^o for equation 48 with the temperature coefficient for equation 49 it was necessary to subtract the heat of dissociation for four moles of iodic acid from the latter. A ΔH^o of 2 kcal. resulted which was 13 kcal. greater than the heat of reaction calculated for reaction 48. It must be remembered that one of the assumptions made in both calculations of the heat of reaction was the constancy of the activity coefficient factor for changes in temperature. The activity coefficients for iodic acid were available only at the freezing points for reaction 48 in which iodic acid was the main solute. An undetermined error was possible in assuming no variation of activity coefficient factor with temperature in both cases, but the calculations at 0°C based on known activity coefficient functions at the freezing points were considered more reliable. In addition it was evident from Figure 21 that differences in the values for the function plotted for 0°C and for 25°C decreased as the ionic strength increased. Since this function represented the deviation of the activity coefficient factor for equation 48 from the limiting law, it was apparent that a dependence on temperature as well as the ionic strength existed. The con-
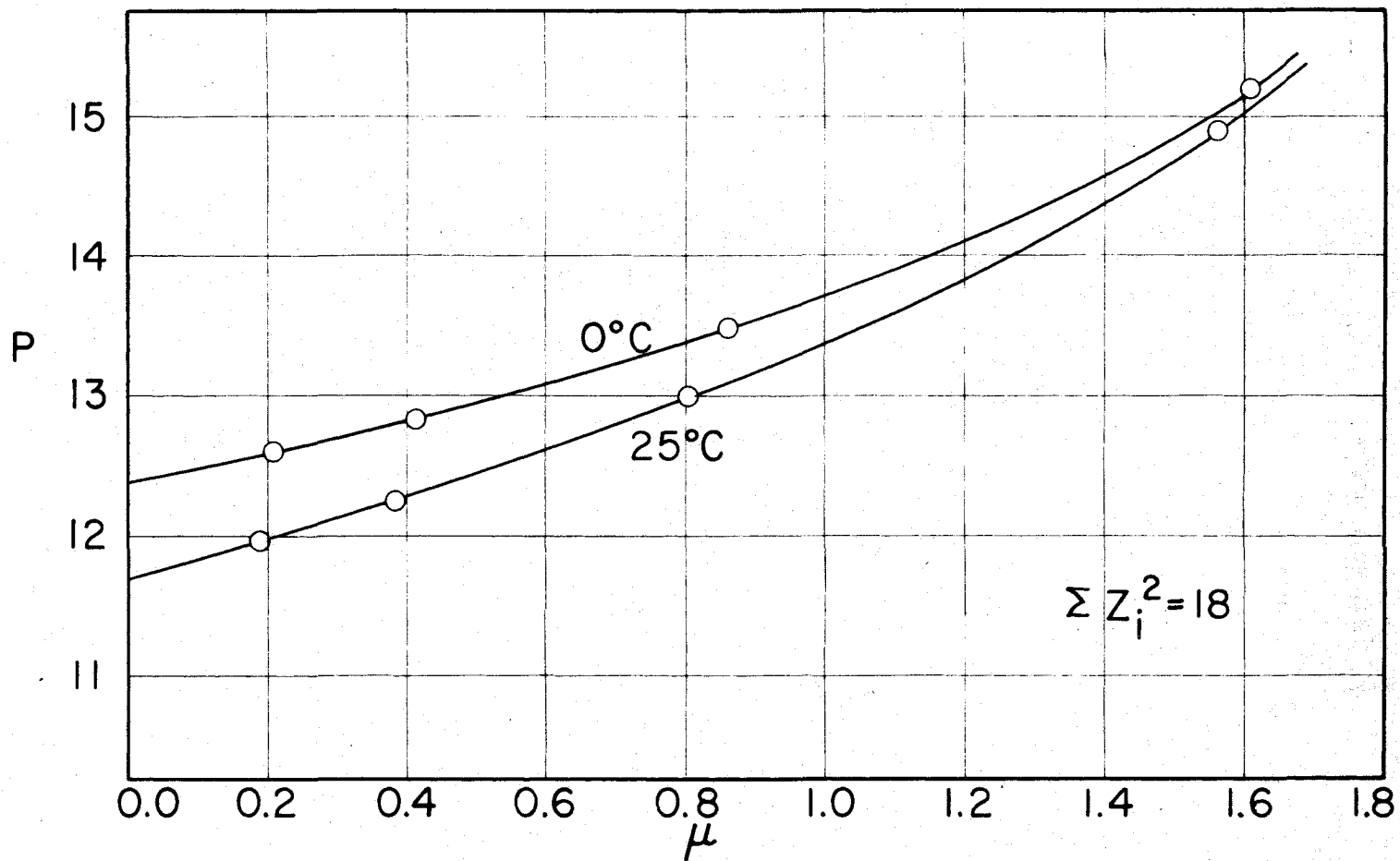
Figure 21. Variation of P With Ionic Strength at $0^{\circ}C$ and $25^{\circ}C$ for a $\sum z_i^2$ of Eighteen.

vergence of the curves in Figure 21 as the ionic strength increased indicated a smaller magnitude of the temperature coefficient for the concentration equilibrium constant at high ionic strength in agreement with the results obtained from $_1K_c$. Accordingly the value of -11 kcal. calculated from the values of K which were obtained by extrapolation to zero ionic strength was considered the best value.

IV. CONCLUSIONS

1. The manganese(II), (III), (IV) equilibrium is rapidly established in iodate solutions at room temperature.

2. The magnitude of the concentration equilibrium constant for this reaction can be determined using a potentiometric titration technique if the constant is large. For conditions under which the constant is small, e.g., less than ten, a colorimetric procedure probably would be satisfactory. Solutions containing manganese(III) and manganese(IV) can be satisfactorily analyzed spectrophotometrically using absorbancy indices determined at two wavelengths in the visible region of the spectrum.

3. The equilibrium reaction for the formation of manganese(III) is dependent on the fourth power of the iodate ion concentration and the third power of the hydrogen ion concentration.

4. The species of the manganese(III) and manganese(IV) oxidation states are negatively charged predominantly.

5. The experimental evidence suggests that the predominant manganese(IV) iodate complex is probably hydrolyzed and contains one oxide, one hydroxide, and four iodate ions. The predominant manganese(III) iodate complex probably is not hydrolyzed.

6. The postulated overall equilibrium reaction may be written:

$$MnO(OH)(IO_3)_4^{---} + Mn^{++} + 3 H^+ 4 IO_3^-$$

$$\rightleftharpoons 2 Mn(IO_3)_4^- + 2 H_2O.$$
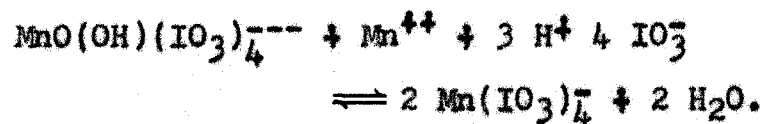
7. No satisfactory method for determining the thermo-dynamic equilibrium constant in concentrated iodic acid solutions has been devised, but an approximate equilibrium constant of 2.5×10^{12} at $0^o C$ was obtained. ΔH^o for the reaction is approximately - 11 kcal.

V. SUMMARY

The manganese(II), (III), (IV) equilibrium in iodate solutions from 0.25 to 1.78 molar has been studied using spectrophotometric and potentiometric titration methods. Colorimetric methods were used for directly analyzing solutions containing manganese(III) and manganese(IV) and for showing that the establishment of the equilibrium was rapid. Potentiometric methods were used to determine the magnitude of the concentration equilibrium constant under various experimental conditions. The equilibrium was found to be dependent on the fourth power of the iodate ion concentration and the third power of the hydrogen ion concentration. Probable formulas for the complex species involved in the equilibrium reaction were postulated and the overall reaction was written as follows:

$$MnO(OH)(IO_3)_4^{---} + Mn^{++} + 3\ H^+ + 4\ IO_3^-$$
$$\rightleftharpoons 2\ Mn(IO_3)_4^- + 2\ H_2O.$$
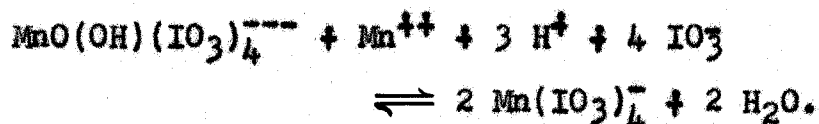
Using activity coefficient data for iodic acid solutions, an approximate equilibrium constant for the above reaction of 2.5×10^{12} at $0°C$ was obtained from a graphical extrapolation of the data to zero ionic strength. A $\Delta H°$ of -11 kcal. was calculated.

VI. LITERATURE CITED

1. Gorgeau, F., _Ann. chim. et phys._ /3_7, 66, 153 (1862).

2. Guyard, A., _Bull. soc. chim. France_ /2_7, 1, 89 (1864).

3. Harcourt, A. V., and W. Esson, _Trans. Roy. Soc._ (London), 156 A, 193 (1866).

4. Tompkins, F. C., _Trans. Faraday Soc._, 38, 131 (1942).

5. Meyer, J., and R. Nerlich, _Z. anorg. u. allgem. Chem._, 116, 117 (1921).

6. Polissar, M. J., _J. Phys. Chem._, 39, 1057 (1935).

7. Polissar, M. J., _J. Am. Chem. Soc._, 58, 1372 (1936).

8. Fessenden, R. W., and B. C. Redmon, _J. Am. Chem. Soc._, 57, 2246 (1935).

9. Launer, H. F., and Yost, D. M., _J. Am. Chem. Soc._, 56, 2571 (1934).

10. Watters, J. I., and I. M. Kolthoff, _J. Am. Chem. Soc._, 70, 2455 (1948).

11. Vetter, K. J., and G. Manecke, _Z. physik. Chem._, 195, 270 337 (1950).

12. Grube, G., and K. Huberich, _Z. Electrochem._, 29, 8 (1923).

13. Bassett, H., and I. Sanderson, _J. Chem. Soc._, 207 (1936).

14. Taube, H., _J. Am. Chem. Soc._, 70, 1216 (1948).

15. Adamson, A. W., _J. Phys. and Colloid Chem._, 55, 293

16. Noyes, R. M., _Trans. N. Y. Acad. Sci._ /2_7, 13, 314 (1951).

17. Bradley, J., and G. Van Praagh, _J. Chem. Soc._, 1624 (1938).

18. McBride, R. S., _J. Am. Chem. Soc._, 34, 393 (1912).

19. Abel, E., _Monatsh._, 80, 455 (1949).

20. Launer, H. F., J. Am. Chem. Soc., 55, 865 (1933).

21. Jordan, P., Helv. Chim. Acta., 34, 699 (1951).

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

23. Heintze, S. G., and P. J. C. Mann, Nature, 158, 791 (1946).

24. Strickland, J. D. H., and G. Spicer, Analytica Chimica Acta, 3, 517 (1949).

25. Waterbury, G. R., A. Hayes, and D. S. Martin, Jr., J. Am. Chem. Soc., 74, 15 (1952).

26. Grube, G., and M. Staesche, Z. Electrochem., 31, 362 (1925).

27. Geloso, M., Acad. Sci., Compt. rend., 202, 1418 (1936).

28. Brenet, J., and A. M. Briot, Acad. Sci., Compt. rend., 232, 726 (1951).

29. Kato, Y., and T. Matuhashi, J. Soc. Chem. Ind. Japan, 34, 312 (1931). /Original not seen; cited in C. A., 26, 563 (1932)_/.

30. Reinitzer, B., and F. Hoffman, Z. anal. Chem., 77, 407 (1929).

31. Travers, A., Acad. Sci., Compt. rend., 182, 972 (1926).

32. Hicks, J., and E. Krockmalski, J. Am. Chem. Soc., 69, 1970 (1947).

33. Cartledge, G. H., and W. P. Ericks, J. Am. Chem. Soc., 58, 2065 (1936).

34. Cartledge, G. H., and P. M. Nichols, J. Am. Chem. Soc., 62, 3057 (1940).

35. Raychondhury, P. C., J. Indian Chem. Soc., 18, 576 (1941).

36. Raychondhury, P. C., J. Indian Chem. Soc., 18, 335 (1941).

37. Olsson, F., Arkiv Kemi, Mineral. Geol., 9, 5 (1924).

38. Berg, M. A., _Acad._ _Sci._, _Compt._ _rend._, _128_, 673 (1899).

39. Mellon, M. G., _Anal._ _Chem._, _21_, 3 (1949).

40. Caster, W. O., _Anal._ _Chem._, _23_, 1229 (1951).

41. Willard, H. H., and H. Diehl, "Advanced Quantitative
      Analysis". New York, N. Y., D. Van Nostrand Com-
      pany, Inc. (1943) p. 376.

42. Müller, E., and O. Friedberger, _Ber._, _35_, 2652 (1902).

43. Willard, H. H., and N. H. Furman, "Elementary Quantita-
      tive Analysis". 3rd. Ed., New York, N. Y., D. Van
      Nostrand Company, Inc. (1940) p. 266.

44. Fowler, R. M., and H. H. Bright, _J._ _Research_ _Nat._ _Bur._
      Standards, _15_, 493 (1935).

45. Scatchard, G., S. S. Prentiss, and P. T. Jones, _J._ _Am._
      Chem. _Soc._, _56_, 805 (1934).

46. Willard, H. H., and L. Greathouse, _J._ _Am._ _Chem._ _Soc._,
      _39_, 2366 (1917).

47. High, J. H., _Analyst_, _68_, 368 (1943).

48. Young, I. G., and C. F. Hiskey, _Anal._ _Chem._, _23_, 506
      (1951).

49. Hayes, A. M., "Chemical Kinetics of the Oxidation of
      Manganese to Permanganate by Periodate. Solubil-
      ity, Activity Coefficients, and Activity Product
      of Manganese(II) Iodate." Unpublished PhD. Thesis.
      Ames, Iowa, Iowa State College Library. (1950).

50. Takacs, I., _Magyar._ _Chem._ _Folyoirat._, _49_, 33, 100
      (1943). /Original not seen; cited in _C._ _A._, _40_,
      6006 (1946)./

51. Pearce, J. N., and V. I. Wirth, _J._ _Am._ _Chem._ _Soc._, _55_,
      3569 (1933).

52. Kolthoff, I. M., and J. J. Lingane, _J._ _Phys._ _Chem._, _42_,
      133 (1938).

53. Laitinen, H. A., "Physical Methods in Chemical Analysis".
      Vol. 2. New York, N. Y., Academic Press Inc.
      (1951) p. 131.

54. Cavanagh, B., J. Chem. Soc., 2207 (1927).

55. Cavanagh, B., J. Chem. Soc., 843 (1928).

56. Kolthoff, I. M., Rec. trav. chim., 47, 397 (1928).

57. Hahn, F. L., and G. Weiler, Z. anal. Chem., 69, 417 (1926).

58. Fuoss, R. M., and C. Kraus, J. Am. Chem. Soc., 55, 476, 2387 (1933).

59. Hayes, A. M., and D. S. Martin, Jr., J. Am. Chem. Soc., 73, 4853 (1951).

60. Abel, E., O. Redlich, and P. Hersch, Z. physik. Chem., 170A, 112 (1934).

61. Groschuff, E., Z. anorg. u. allgem. Chem., 47, 331 (1905).

62. Kraus, C. A., and H. C. Parker, J. Am. Chem. Soc., 44, 2429 (1922).

63. Schumb, W. C., and S. B. Sweetser, J. Am. Chem. Soc., 57, 871 (1935).

64. Duke, F. R., J. Am. Chem. Soc., 69, 2885 (1947).

VII. ACKNOWLEDGEMENTS