Effect of Ionic Strength.—K_1 was determined for the zinc chelate in the absence of any salt, as well as in 0.15 M sodium nitrate. The stability constant in the former case is 213 as compared to 229 (Table II). Little sensitivity to ionic strength is to be expected for an isoelectric reaction such as that represented by equation (1).

Effect of Temperature.—The stability constant for the zinc chelate was measured at 35° ($K_1 = 2.08 \times 10^2$) as well as at 25° ($K_1 = 2.29 \times 10^2$). The drop with increasing temperature is small but significant. The enthalpy change in the formation of the complex, calculated from the equation

$$\mathrm{d} \ln K/\mathrm{d}T = \Delta H^\circ/RT^2 \qquad (7)$$

is −1750 cal./mole. Since at 25° the free energy change for the reaction is

$$\Delta F^\circ = -RT \ln K = -3200 \text{ cal./mole} \qquad (8)$$

the entropy change may be computed to be

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T} = 4.8 \text{ cal./mole deg.} \qquad (9)$$

The positive sign and the magnitude of ΔS° are consistent with a more detailed picture of reaction (1)

$$\mathrm{Zn(H_2O)_4^{++} + D = Zn(H_2O)_2D + 2H_2O} \qquad (10)$$

in which the chelate is assumed to displace two water molecules and thus produce a net increase of one in the number of molecules present.

Conclusion.—The chelates of pyridine-2-azo-*p*-dimethylaniline thus possess many of the characteristics desirable for measurements of formation constants of metal complexes of moderate stability. (1) The extinction coefficient of the dye is very high so that its concentration can be kept so small as to exert no appreciable influence on the cation equilibrium of interest. (2) The absorption peak is shifted appreciably when the dye forms a complex with the cation. (3) For many cations the stability constant is not dependent on *p*H within a suitably chosen range. (4) The stability constants are relatively insensitive to changes in temperature or ionic strength. (5) The magnitudes of the stability constants are not too high.

Limitations in application may arise, nevertheless, from a number of causes. For complexes of high stability, other colored chelates[2,3] must be used, since the stability constant of the metal–dye combination must be of the order of magnitude of the complex under investigation if maximum precision is to be obtained. Furthermore, the range of *p*H in which this particular azopyridine dye can be conveniently used is fairly restricted, particularly if hydrolytic equilibria of the metal became significant. Finally, the dye chelate, in principle, may complex further with other ligands in solution; the seriousness of this complication must be examined in each individual system.

This investigation was supported in part by a grant from the Rockefeller Foundation.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Manganese(II), -(III), -(IV) Equilibrium in Iodic Acid[1]

BY GLENN R. WATERBURY AND DON S. MARTIN, JR.

RECEIVED JANUARY 16, 1953

The equilibrium of the disproportionation reaction of manganese(III) has been measured in various aqueous iodate systems by a potentiometric titration method. The dependence of the equilibrium state upon iodate ion, hydrogen ion and iodic acid concentrations and upon the ionic strength and temperature has been studied. The behavior indicates the equilibrium: $\mathrm{Mn^{IV} + Mn^{II} + 4IO_3^- + 3H^+ \rightleftarrows 2Mn^{III}}$, is rapidly established, and equilibrium constants are reported for this reaction. A colorimetric procedure has been developed for the analysis of iodate solutions of manganese(III), -(IV). The possible ionic species contributing to the equilibrium are discussed.

Introduction

In a previous study of the kinetics for the well-known periodate oxidation of manganese(II) to permanganate[2] a mechanism was postulated which assumed a rapid establishment of the equilibrium

$$\mathrm{Mn^{II} + Mn^{IV} \rightleftarrows 2Mn^{III}} \qquad (1)$$

Various investigators have postulated the existence of the equilibrium in systems containing complexing agents such as fluoride, oxalate, phosphate and sulfate ions. Several studies[3–10] of the rapidity of the establishment of the equilibrium have been made, and measurements of the equilibrium constant have been made by Grube and co-workers for systems containing sulfuric acid[11a] and phosphoric acid.[11b] In both these cases the equilibrium constants were calculated from the potential difference between a solution containing equal concentrations of manganese(III) and manganese(II), and a solution containing equal concentrations of manganese(III) and manganese(IV). In the most dilute acid solutions studied they obtained the equilibrium constants for reaction 1:14.3 at 12° in 4.55 M $\mathrm{H_2SO_4}$ and 1.25×10^4 at 17° in 3.33 M $\mathrm{H_3PO_4}$. The equilib-

---

(1) Contribution No. 239 from the Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa. Work was performed in the Ames Laboratory of the Atomic Energy Commission.

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

(3) F. C. Tompkins, *Trans. Faraday Soc.*, **38**, 131 (1942).

(4) J. Meyer and R. Nerlich, *Z. anorg. allgem. Chem.*, **116**, 117 (1921).

(5) M. J. Polissar, *J. Phys. Chem.*, **39**, 1057 (1935).

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

(7) R. W. Fessenden and B. C. Redmon, *ibid.*, **57**, 2246 (1935).

(8) H. F. Launer and D. M. Yost, *ibid.*, **56**, 2571 (1934).

(9) J. I. Watters and I. M. Kolthoff, *ibid.*, **70**, 2455 (1948).

(10) K. J. Vetter and G. Manecke, *Z. physik. Chem.*, **195**, 270, 337 (1950).

(11) (a) G. Grube and K. Huberich, *Z. Elektrochem.*, **29**, 8 (1923); (b) G. Grube and M. Staesche, *ibid.*, **31**, 362 (1925).

rium constants were greater in the more concentrated solutions of each acid.

In the kinetics work moderately stable solutions of manganese(III) and manganese(IV) were prepared in high iodic acid concentrations, and a potentiometric titration method has been found to be suitable for the determination of the equilibrium constants for reaction 1 in these solutions. A study of the factors influencing the equilibrium was made, and the over-all equilibrium reaction was postulated.

Experimental

Materials.—Periodic acid, iodic acid and potassium hydrogen iodate of reagent quality, supplied by the G. Frederick Smith Co., were used in these studies. The potassium hydrogen iodate served as a primary standard for acidimetric and iodometric titrations. The purities of the other reagents met A.C.S. standards, and the solutions were standardized by conventional analytical methods.

Manganese(II) solutions were prepared by adding the sulfate to an iodic acid solution to saturate it with manganese(II) iodate. Any slight excess of manganese(II) iodate which precipitated was removed by filtering through a fine sintered glass filter. Since the concentration of the sulfate ion introduced by this procedure was approximately 10^{-4} *M* in 0.25 to 1.8 *M* iodic acid, the effect of sulfate on the measurements was considered negligible. In attempts to prepare the solutions by dissolving manganese metal directly in warm iodic acid, the manganese(II) was partially oxidized to manganese(III), and reduction of some iodic acid occurred. A slow oxidation occurred in manganese(II) solutions at room temperature, and only fresh solutions, which gave no detectable absorption besides that of the iodic acid, were used.

It was not possible to prepare pure manganese(IV) iodate solutions; in all cases either manganese(III) or permanganate was present in discernible concentrations. Of the methods tried, the one involving dissolution of freshly prepared hydrous manganese dioxide in iodic acid and the subsequent careful oxidation of most of the manganese(III) to manganese(IV) with periodic acid was the most successful; the preparation of a manganese(IV) solution containing very small amounts of manganese(III) and no excess periodic acid proved very difficult. The solutions were filtered through fine sintered glass and diluted, and the solutions finally obtained exhibited no Tyndall effect. Solutions of manganese(IV) were amber or brown, but the color changed to violet as the manganese(IV) was reduced to manganese(III); this reduction occurred spontaneously over a period of several days if the solutions were left exposed to the air. No decomposition was evident for solutions in closed quartz containers, but a red-brown precipitate formed if the containers were glass. Spectrographic analysis and the general appearance of the precipitate indicated that it was the insoluble double iodate, $K_2Mn(IO_3)_6$; compounds of this type were described originally by Berg.[12] Solutions containing lithium or sodium produced yellow precipitates upon standing for several days, but the precipitation was sufficiently slow that the solutions were usable in the titrations. Berg[12] stated that sodium does not form a double iodate similar to the potassium precipitate, but Olsson[13] described double iodates of the alkali metals as the yellow to yellow brown precipitates, $M_2Mn(IO_3)_5$.

Colorimetric Analyses.—Since the higher oxidation states of manganese absorb highly in the visible region of the spectrum even in dilute solutions, the manganese(II) solutions were assumed to be pure if no absorption in excess of that of iodic acid could be detected on a Cary recording spectrophotometer. The concentrations of these solutions were determined by evaporating aliquots to dryness with sulfuric acid to remove the iodic acid, oxidizing the manganese to permanganate with periodic acid, and comparing the absorption with standard samples.[14] The total manganese concentration was taken to equal the manganese(II) concentration. Concentrations of manganese(III) as low as 3.0×10^{-6} *M* could be detected using 5-cm. cells which would limit the error of this method to better than 2% for manganese(II) solutions of 2.00×10^{-4} *M*.

The amounts of manganese(III) and manganese(IV) in the solutions could not be determined by any simple oxidation–reduction titrimetric procedure because of interference by the large amounts of iodic acid. Since the species are colored, a colorimetric procedure was developed. Neither manganese(III) nor manganese(IV) was prepared pure so the absorbancy indices could not be determined directly. (The absorbancy of a solution, A, is defined by $A = \log_{10} I_0/I$ where I_0 and I are the intensity of the light passing through the blank and sample cells, respectively. The relation is used to give the molar absorbancy index, a_m, $A = a_m cd$, where c is concentration in moles per liter and d is the cell thickness in centimeters.)

Standardized solutions of manganese(II) were scanned spectrophotometrically between 4000 and 7000 Å. after each addition of small increments of periodic acid; the high absorbancy of iodic acid interfered below 4000 Å. The solutions were heated to ensure complete reaction, and the volume maintained constant by adding to the cooled solutions water to replace the evaporation. In this way a series of absorption spectra were obtained for various mixtures of manganese(II), -(III), -(IV) and permanganate. Curve 3 of Fig. 1 shows the broad peak with maximum at 5300 Å. due to manganese(III). Further oxidation would give a spectrum such as curve 1 of Fig. 1. Still more oxidation would give spectra in which the characteristic twin maxima and the minima of permanganate were apparent. Curve 1 represents a spectrum in which the presence of the permanganate component can barely be discerned. Using the molar absorbancy index of 2240 moles^{-1} liter cm.$^{-1}$ at 5260 Å. for the Cary spectrophotometer,[1] the concentration of permanganate was estimated to be 0.023×10^{-4} *M* for this solution, just 0.8% of the total manganese content determined by analysis. The molar absorbancy index on the basis of the remaining manganese was calculated for 4300 and 5260 Å. These values were attributed to the manganese(IV) component. With them, the corresponding absorbancy indices for manganese(III) were obtained from the spectra of manganese(III), -(IV) mixtures and the total manganese analyses. Since the equilibrium constant for reaction 1 in these solutions was large as will be apparent later, the molar absorbancy indices could be tested for consistency over a range of manganese (III), -(IV) concentration ratios with negligible quantities of manganese(II) present. Completely consistent results for the number of solutions tested were obtained using the following molar absorbancy indices obtained in this manner: 1370 and 320 liters moles^{-1} cm.$^{-1}$ at 4300 and 5260 Å., respectively for manganese(IV) and 101 liters moles^{-1} cm.$^{-1}$ at 5260 for manganese(III).

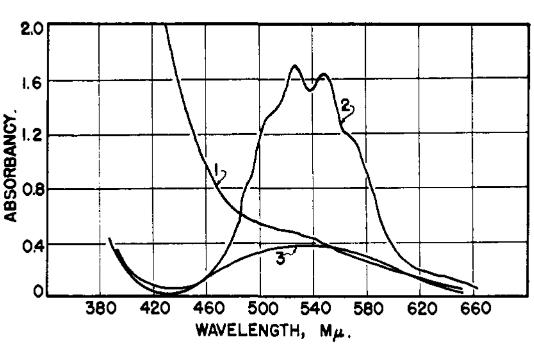

Fig. 1.—Adsorption characteristics of aqueous solutions of various manganese oxidation states on the Cary spectrophotometer: 1, 2.82×10^{-4} *M* manganese(IV) and 0.023×10^{-4}*M* permanganate in 1.00 *M* iodic acid, 5-cm. cell; 2, 7.59×10^{-4} *M* permanganate, 1-cm. cell; 3, manganese (III), -(II) solution, 3.85×10^{-4} *M* in 1.00 *M* iodic acid.

All the manganese(III), -(IV) solutions in this work were analyzed utilizing these values by taking absorbancy readings at 4300 and 5260 Å. When necessary, the manganese-

---

[12] M. A. Berg, *Compt. rend.*, **128**, 673 (1899).

[13] F. Olsson, *Arkiv Kemi, Mineral. Geol.*, **9**, 5 (1924).

[14] H. H. Willard and L. H. Greathouse, THIS JOURNAL, **39**, 2366 (1917).

(II) content was obtained by difference from the total manganese content measured colorimetrically by the periodate oxidation method.

Procedure.—The equilibrium was established too rapidly to be measured spectrophotometrically. Qualitatively, the amber or brown manganese(IV) solutions turned violet immediately upon mixing with manganese(II). Exploratory experiments in 1 *M* iodic acid solution showed that the equilibrium constant for reaction 1 was very large and could not be measured by a spectrophotometer method.

In the determination of the equilibrium constants from cell potentials, a large constant and the corresponding large potential difference is advantageous. The general procedure followed was to add small amounts of manganese(III), -(IV) iodate solution from a microburet to a rapidly stirred solution of manganese(II) and to measure the potential after each addition. The effects of hydrogen ion, manganese, iodate and iodic acid concentrations as well as temperature and ionic strength were investigated by conducting titrations in which all but one or two of the variables were held constant. In some cases perchloric acid and lithium perchlorate were used to adjust ionic strength and hydrogen ion concentration. The conditions of the experiments are given in Table I; in each experiment duplicate or triplicate titrations were made.

The total volume of the additions in the titration were relatively large. However, 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. In this way the conditions of the experiment remained constant. In a few experiments the procedure was reversed and the manganese(II) iodate was used as the titrating solution. The end results obtained using either procedure were identical.

Potential measurements were made using a Beckman model G *p*H meter as a potentiometer after each addition of titrating solution. The cell was of the type

$$\left.\begin{array}{l}\text{Pt; Mn}^{\text{II}}\text{, Mn}^{\text{III}}\text{, HIO}_3(C_1)\text{: HIO}_3(C_1)\text{, AgIO}_3\text{; Ag}\\ \text{Pt; Mn}^{\text{II}}\text{, Mn}^{\text{III}}\text{, HIO}_3(C_1)\text{: HIO}_3(C_1)\text{, AgIO}_3\text{; Ag}\end{array}\right]$$

Since the differences between two potential readings was of importance rather than the accurate determination of one value, the double cell proved advantageous. 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 was 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 canceled the first.

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 silver–silver iodate half cells were prepared using similar solutions instead of iodic acid.

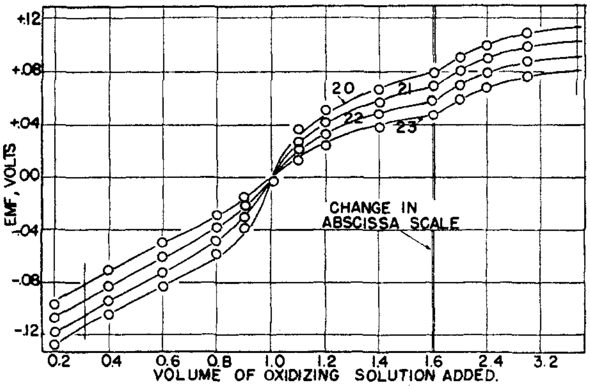

Fig. 2.—Potentiometric titration curves of manganese(II) by manganese(III), -(IV) solutions in 1.00_0 *M* perchloric acid and 1.00_0 *M* lithium perchlorate: 20, 1.00_0 *M* HIO$_3$; 21, 0.80_0 *M* HIO$_3$; 22, 0.64_0 *M* HIO$_3$; 23, 0.50_0 *M* HIO$_3$.

TABLE I

SOLUTION STRENGTHS AND TEMPERATURES FOR THE POTENTIOMETRIC TITRATIONS

[HIO$_3$]^a	[Mn^{II}] × 10^4	[HClO$_4$]	[Mn^{IV}] × 10^4	f^b	[LiClO$_4$]	Temp., °C.	K_c
0.990	1.84		6.56	0.287		00.0	$7.4_4 \times 10^4$
.990	1.84		4.12	.287		00.0	$7.4_4 \times 10^4$
.990	1.84		5.16	.287		23.4	$1.5_3 \times 10^4$
.990	1.84		5.16	.287		44.8	$3.7_6 \times 10^3$
.990	1.84		5.06	.298		24.3	$1.5_1 \times 10^4$
.990	1.78		5.16	.287		24.3	$1.5_1 \times 10^4$
.990	1.78		5.33	.281		57.2	$2.2_9 \times 10^3$
.497	1.70		7.76	.067		00.0	$3.3_9 \times 10^4$
.497	1.70		2.50	.239		00.0	$3.3_9 \times 10^4$
.497	1.70		2.50	.239		22.5	$5.8_9 \times 10^3$
.497	1.70		2.50	.239		43.5	$1.4_4 \times 10^3$
.497	1.70		2.50	.239		61.5	$5.6_9 \times 10^3$
1.782	2.04		4.17	.595		00.0	$3.2_3 \times 10^5$
1.782	2.04		4.17	.595		47.3	$2.2_4 \times 10^4$
1.782	2.04		4.17	.595		22.8	$8.1_2 \times 10^4$
1.782	2.04		4.17	.595		64.5	$9.3_3 \times 10^3$
0.249	1.02		1.85	.503		00.0	$6.6_8 \times 10^3$
0.249	1.02		1.85	.503		21.5	$1.1_4 \times 10^5$
1.000	1.80	2.00_0	6.26	.066		23.4	$5.5_1 \times 10^3$
1.000	1.80	2.00_0	5.65	.066		23.4	$5.5_1 \times 10^3$
0.80_0	1.44	2.00_0	5.33	.066		23.4	$2.3_3 \times 10^3$
$.80_0$	1.44	2.00_0	3.03	.066		23.4	$2.3_3 \times 10^3$
$.64_0$	1.66	2.00_0	5.31	.066		23.4	$9.8_4 \times 10^3$
$.64_0$	1.66	2.00_0	4.05	.120		23.4	$9.8_4 \times 10^3$
$.50_0$	1.44	2.00_0	2.77	.199		23.4	$3.9_0 \times 10^3$
$.50_0$	1.44	2.00_0	2.81	.066		23.4	$3.9_0 \times 10^3$
1.00_0	1.80	1.00_0	5.21	.199	1.00_0	23.4	$6.9_7 \times 10^3$
0.80_0	1.44	1.00_0	4.17	.199	1.00_0	23.4	$3.1_7 \times 10^5$
0.64_0	1.15	1.00_0	3.33	.199	1.00_0	23.4	$1.3_4 \times 10^3$
0.50_0	0.90	1.00_0	2.60	.199	1.00_0	23.4	$5.6_7 \times 10^3$
1.00_0	1.60	1.50_0	5.53	.193	0.50_0	23.4	$2.7_2 \times 10^3$
1.00_0	1.60	1.50_0	5.33	.193	0.50_0	23.4	$2.7_2 \times 10^3$
1.00_0	1.56	2.00_0	4.36	.467		0.00	$2.0_7 \times 10^4$

[a] [HIO$_3$] indicates the molar concentration (moles/liter).
[b] See equation 4.

Temperature control of ±0.2° was attained by placing the reaction vessel in a water-bath thermostat. The titrating solution was added in sufficiently small increments that no sudden change in temperature was observed. The large number of potentials measured in this manner permitted the plotting of smooth titration curves. A typical set of curves is shown in Fig. 2 in which the abscissa represents the ratio of the volume of oxidant added to the volume equivalent of reductant. The smooth curves represent the experimental data which included as many as 30–40 potential determinations. The circles represent the potentials calculated from the finally selected equilibrium constants by the method given below.

Attempts to isolate the iodate dependence by using 1 *M* lithium iodate in neutral solutions were unsuccessful since the equilibrium constant for reaction 1 was too low under these conditions. Thus, a dependence on hydrogen ion was discovered. It was found by qualitative visual tests that a hydrogen ion concentration of approximately 0.07 *M* was required before the violet color due to manganese(III) could be discerned in the titrations. Consequently, it was necessary to keep the acidity sufficiently high with perchloric acid that it remained about constant during the studies on iodate dependence.

The nature of the complexes in solution was investigated by observing the movement of the manganese(III) and manganese(IV) species during electrolysis. The visible boundary between a violet manganese(III) solution in 1 *M* iodic acid and a 1 *M* iodic acid solution moved toward a platinum anode and away from the cathode. Similar results were obtained for a brown manganese(IV) solution in iodic acid and lithium iodate. It was concluded that both the manganese(III) and manganese(IV) species were negatively charged.

Treatment of Data.—The titration curves obtained were not symmetrical about the end-point, and a graphical method in which the evolute or locus of centers of curvature of the experimental titration curve was constructed, as described by Hahn and Weiler, was used to determine the end-point.[15] A straight line which was drawn asymptotically tangent to the two branches of the evolute cut the original titration curve at the end-point.

Preliminary equilibrium constants were estimated from the potential breaks. The actual constants were obtained by comparing the entire experimental curves with theoretical curves, the points of which were calculated in the following manner assuming that no polymerization of the manganese species occurred.

If p was the original amount of manganese(II) being titrated, m was the manganese(IV) added, and x, the manganese(II) or manganese(IV) which had reacted, then the following equations applied

$$\begin{array}{ccc} \mathrm{Mn^{II}} + \mathrm{Mn^{IV}} & \rightleftarrows & 2\mathrm{Mn^{III}} \\ (p - x)\ (m - x) & & 2x \end{array} \qquad (2)$$

The concentration equilibrium constant for the reaction was

$$K_c = \frac{[\mathrm{Mn^{III}}]^2}{[\mathrm{Mn^{II}}][\mathrm{Mn^{IV}}]} = \frac{(2x)^2}{(p - x)(m - x)} \qquad (3)$$

If the ratio of the manganese(III) to manganese(IV) in the titrating solution was f, then the expression became

$$K_c = (2x + fm)^2/(p - x)(m - x) \qquad (4)$$

This quantity was 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 any given titration solution. In terms of the above symbols the Nernst equation was

$$E = E^0 - (RT/F)\ln\,[a_{\mathrm{Mn}^{+++}}/a_{\mathrm{Mn}^{++}}] = E^0 - (RT/F)\ln\left[\frac{(2x + fm)\gamma_{\mathrm{MnIII}}}{(p - x)\gamma_{\mathrm{MnII}}}\right] \qquad (5)$$

When y was set equal to m/p and the Nernst equation was written in terms of y, f and K_c, the following working form was obtained

$$E = \text{constant} - \frac{RT}{F}\ln\frac{-2K_c\,\{1 + y + fy - [(1 - y)^2 + (8fy + 8fy^2 + 4f^2y^2 + 16y)/K_c]^{1/2}\}}{8 - K_c\,\{1 - y - 4fy/K_c + [(1 - y)^2 + (8fy + 8fy^2 + 4f^2y^2 + 16y)/K_c]^{1/2}\}} \qquad (6)$$

The estimated K_c values from the experimental curves were used in the above equation, and points for corresponding theoretical plots were calculated. The calculations were repeated with adjustments in K_c to give the best fit with the experimental curves. In most cases the experimental and calculated curves were superimposable; a few small deviations observed especially in that portion of the curve immediately preceding or following the greatest change in potential were of the magnitude of the expected experimental error. The equilibrium constant for the theoretical curves which most closely matched the entire experimental curves are listed in Table I. In titrations for which the equilibrium constant was 10^3 or less and for a large f, *e.g.*, 0.5, the titration error or the difference between the inflection point of the curve and the equivalence point made the matching of the calculated and experimental curves difficult. For K_c values of 10^3 and 10^4 and a f of 0.5, the second derivative of E, equation 6, with respect to y was calculated to equal zero at y values of 0.967 and 0.997, respectively. Since the equivalence point was at y equal to one, errors of 3.3 and 0.3%, respectively, in the selection of the stoichiometric end-point would have been introduced.

In making duplicate or triplicate titrations, the total manganese concentration was changed between determinations, but no change in the equilibrium constant was evident. It was concluded that there was no polymerization of any manganese species in the iodate solutions.

The equilibrium constant, K_c, was applicable only for the particular set of experimental conditions imposed during the titration. The variations in K_c with the iodate ion and hydrogen ion concentrations, ionic strength and temperature gave some information about the actual equilibrium involved.

The effect of iodate and hydrogen ion concentrations were investigated separately in the series of titrations in which the ionic strength was maintained effectively constant by using lithium perchlorate and perchloric acid mixtures with a total concentration of 2 M (see Table I). 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 which was in no case less than 1 M. This dissociation constant for HIO_3, as given by Fuoss and Kraus,[16] is 0.168 at 25°; therefore the hydrogen ion concentration remained approximately equal to the perchloric acid strength of 1 or 2 M, and the iodate ion existed in low concentrations which were approximately proportional to the concentration of iodic acid. To test the influence of the activity coefficient factor in the expression

$$K_a = \frac{[\mathrm{H^+}][\mathrm{IO_3^-}]}{[\mathrm{HIO_3}]}\,\frac{\gamma_{\mathrm{H^+}}\gamma_{\mathrm{IO_3^-}}}{\gamma_{\mathrm{HIO_3}}} \qquad (7)$$

the concentration of iodate was calculated using values for this factor of 0.2, 0.67, 1.0 and 5.0. Plots of the log K_c against log $[\mathrm{IO_3^-}]$ for each perchloric acid concentration and assumed activity coefficient factor, as shown in Fig. 3, all gave slopes between 3.91 and 4.09. Since these large variations in the activity coefficient factor did not change the slope of the lines materially, the calculated iodate concentrations were satisfactorily proportional to the true concentrations, and a fourth power dependence on iodate concentration was indicated.

With the above values for iodate dependence it was possible to use the data in Table I for establishing the hydrogen ion dependence also. log K_c − 4 log $[\mathrm{IO_3^-}]$ was plotted against log $[\mathrm{H^+}]$ as shown in

---

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

(16) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476, 2387 (1933).

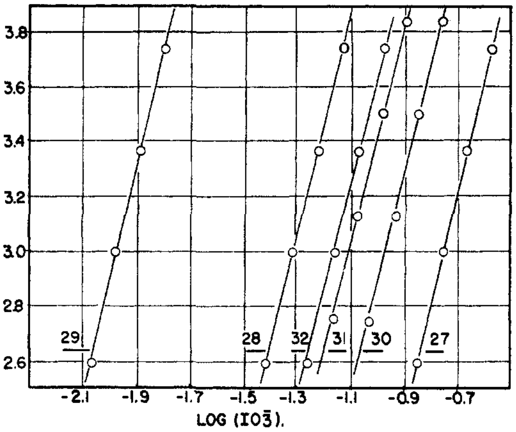

Fig. 3.—The variation of the equilibrium constant, K_c, with iodate ion concentration: 27, 0.2 activity cofficient factor, 2 *M* HClO₄; 28, 1.0 activity coefficient factor, 2 *M* HClO₄; 29, 5 activity coefficient factor, 2 *M* HClO₄; 30 0.67 activity coefficient factor, 1 *M* HClO₄; 31, 1.0 activity coefficient factor, 1 *M* HClO₄; 32, 0.67 activity coefficient factor, 2 *M* HClO₄.

Fig. 4. Since 0.67 was believed to be the most reasonable value for the activity coefficient factor, this value as well as 1.0 was used to calculate the iodate concentrations in these plots. The values used did not critically influence the slope which was found to be 2.92 and 3.04 in the two cases; a third power dependence on hydrogen ion concentration was indicated. The over-all reaction became

$$\mathrm{Mn^{IV} + Mn^{II} + 4IO_3^- + 3H^+ \rightleftharpoons 2Mn^{III}} \quad (8)$$

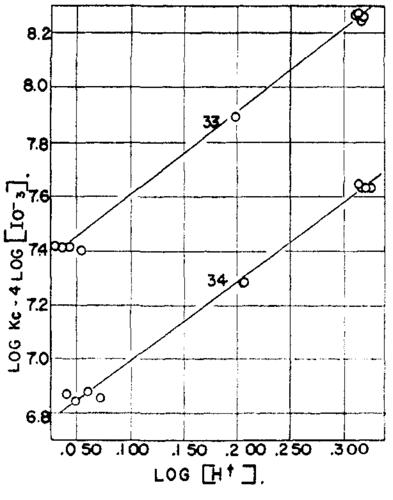

Fig. 4.—The variation of the concentration equilibrium constant, K_c, with hydrogen ion concentration: 33, 1.0 activity coefficient factor; 34, 0.67 activity coefficient factor.

The nature of the manganese species involved has not been indicated; however, some interesting speculation was possible. The existence of more than one species of each oxidation state was a possibility, but no evidence was found indicating the presence of more than a single species for each state under the conditions employed in this work. Manganese(II) has been shown to be negligibly hydrolyzed.[17] The solubility of manganese(II) iodate measured by Hayes and Martin[18] was somewhat higher in iodate solutions than would correspond to a simple 2–1 electrolyte. From those values a rough equilibrium constant was estimated for the reaction

$$\mathrm{Mn^{++} + IO_3^- \rightleftharpoons Mn(IO_3)^+},\ K = 0.09 \quad (9)$$

On the basis of this constant it was concluded that for the determinations of K_c made in the perchloric acid solutions the predominant species of the manganese(II) was the simple hydrated $\mathrm{Mn^{++}}$ ion. In the colorimetric analyses of the manganese(III), -(IV) solutions it was found that in all solutions tested the results were consistent with the total manganese analyses although the iodic acid, perchloric acid, and lithium perchlorate concentrations varied over a considerable range. Either the formation of different species did not alter the absorption characteristics of the solution or a single species dominated each oxidation state. The range of concentrations tested was perhaps insufficient to determine the constancy of the iodate and hydrogen ion dependencies, but unless single species dominated each oxidation state the observation of integral values both for the powers of the hydrogen ion concentration and iodate ion concentration dependences would be high fortuitous. The equilibrium reaction was written using the general formulas as

$$\mathrm{[Mn^{IV}(O)_{\mathit{p}}(OH)_{\mathit{q}}(IO_3)_{\mathit{r}}]^{-v} + Mn^{++} + 3H^+ + 4IO_3^- \rightleftharpoons 2[Mn^{III}(IO_3)_{\mathit{n}}(OH)_{\mathit{m}}]^{-w} + \mathit{s}H_2O} \quad (10)$$

For this general equation n must be equal to $(4 + r)/2$ and m equal to $(2p + q - 3)/2$. If a maximum coördination number of six was assumed for manganese, further restrictions were imposed upon the possible values for the subscripts. The magnitudes of the negative charges on the species were not known, but an indication of the values for v and w was inferred by a consideration of the variation of the concentration equilibrium constant with ionic strength.

In the solutions containing iodic acid with no perchloric acid or lithium perchlorate the effect of ionic strength, μ, was not simply resolved since the degree of ionization of iodic acid as well as the activity coefficients of the species indicated in equation 10 depended on the ionic concentration. Abel, Redlich and Hersch[19] have reported activity coefficients for iodic acid solutions from 0.001 to over 10 molal from freezing point determinations. Using the degree of dissociation calculated from these activity coefficient data and densities for iodic acid, reported by Groschuff[20] and Kraus and Parker,[21] the actual iodate ion concentrations were calculated. Since the hydrogen and iodate ion concentrations were equal in the iodic acid solutions, the expression for the equilibrium constant

$$K = \frac{[\mathrm{Mn^{III}}]^2\,\gamma^2_{\mathrm{Mn^{III}}}}{[\mathrm{Mn^{II}}]\,[\mathrm{Mn^{IV}}][\mathrm{H^+}]^3[\mathrm{IO_3^-}]^4\,\gamma_{\mathrm{Mn^{II}}}\gamma_{\mathrm{Mn^{IV}}}\gamma^3_{\mathrm{H^+}}\gamma^4_{\mathrm{IO_3^-}}} \quad (11)$$

---

(17) R. K. Fox, D. F. Swinehart and A. B. Garrett, THIS JOURNAL, **63**, 1779 (1941).

(18) A. M. Hayes and D. S. Martin, Jr., *ibid.*, **73**, 4853 (1951).

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

(20) E. Groschuff, *Z. anorg. Chem.*, **47**, 331 (1905).

(21) C. A. Kraus and H. C. Parker, THIS JOURNAL, **44**, 2429 (1922).

when written in logarithmic form became

$$\log K = \log K_c - 7 \log [IO_3^-] + \log \Gamma \quad (12)$$

where Γ indicated the activity coefficient factor. Using a treatment similar to that described by Schumb and Sweetser,[22] an extended form of the Debye–Hückel equation was used to express the activity coefficient factor, and the equilibrium constant was written in the form

$$\log K = \log K_c - 7 \log [IO_3^-] - A\Sigma z_i^2 (\mu)^{1/2} + C\mu \quad (13)$$

where A is a constant equal to 0.488 for aqueous solutions at 0°,[23] C was a composite constant made up of the various C_i's for the individual ions, and Σz_i^2 was the difference between the sum of the squares of the charges on the products in the reaction and the sum of the squares for the reactants. Thus when $[\log K_c - 7 \log [IO_3^-] - A\Sigma z_i^2(\mu)^1/_2]$, designated as P for convenience, was plotted against the ionic strength, a straight line should have been obtained insofar as the extended Debye–Hückel equation described the activity coefficients, and the slope of the line should be opposite in sign from Σz_i^2. With an extrapolation to zero ionic strength, the intercept should have given the value of log K.

Since the formulas and charges of the manganese(III) and manganese(IV) species in equation 10 were unknown, Σz_i^2 also was not known. Consequently a series of values of P were calculated for various values of Σz_i^2 in the range 0 to −30. Plots of P against μ were made for 0° in Fig. 5. Values of Σz_i^2 between −16 and −24 produced curves which closely approximated straight lines. With this information the various combinations of the subscripts which included iodate in both the manganese(III) and manganese(IV) species and indicated a coördination number less than seven for manganese were tried in equation 10. Four possible combinations were found; three gave Σz_i^2 values of −18; and the fourth gave a value of −28. Only one of the cases, for which Σz_i^2 was −18, gave a manganese(III) species which was not hydrolyzed. Since it seems improbable that the manganese(III) complex was hydrolyzed in the strongly acid solutions used, the reaction represented in equation 15 was proposed as the most likely possibility.

$$[MnO(OH)(IO_3)_4]^{---} + 3H^+ + 4IO_3^- + Mn^{++} \rightleftarrows 2[Mn(IO_3)_4]^- + 2H_2O \quad (15)$$

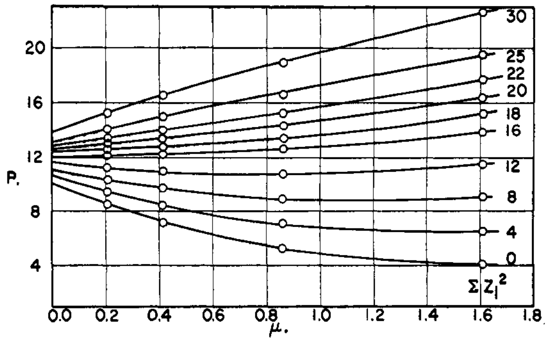

Fig. 5.—Variation of P with ionic strength of various Σz_i^2 values at 0°.

In the case of the oxalate system, Duke reported evidence that hydroxylated manganese(III) complexes did not exist.[24] In the iodic acid solutions it appears possible that significant amounts of manganese(II) exists in the form of the $Mn(IO_3)^+$ complex so the iodate dependence indicated in equation 15 may be questioned. When the $4IO_3^- + Mn^{++}$in this equation were replaced by $3IO_3^- + Mn(IO_3)^+$, the conclusions regarding the nature of the manganese(III) and manganese(IV) species were unchanged by the necessary modifications of the above treatment.

The possibilities of a higher coördination number for manganese, a hydrolyzed manganese(III) species and a manganese(II) complex prevented making a definite statement of the actual reaction. It is interesting to note that Taube has suggested recently a possible coördination number of four for manganese(III) based on a $d^1d^1d^1d^1$ DSP^2 electronic state.[25]

Log K_c values at 25° were taken from the approximately straight line plots of log K_c against $1/T$ for titrations in which the main solute was iodic acid. Calculations of concentrations were made assuming activity coefficient factors independent of temperature between 0 and 25°. The intercepts for the plots of P against μ at 0 and 25° were 12.4_0 and 11.6_8 which indicated the thermodynamic constants for equation 14 were approximately 2.5×10^{12} and 4.8×10^{11}, respectively, corresponding to a ΔH^0 of about −11 kcal. Due to the uncertainty in the selection of the correct charge of the complex species and in the many assumptions, this can be considered only an approximate value.

AMES, IOWA

---

[22] W. C. Schumb and S. B. Sweetser, THIS JOURNAL, **57**, 871 (1935).

[23] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 587.

[24] F. R. Duke, THIS JOURNAL, **69**, 2885 (1947).

[25] H. Taube, *Chem. Revs.*, **50**, 69 (1952).