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Authors
Hugus, Z.Z.
Latimer, W.M.

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THE HEAT OF OXIDATION OF MANGANOUS ION TO PERMANGANATE
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Z. Z. Hugus and W. M. Latimer

Radiation Laboratory, Department of Chemistry and Chemical Engineering
University of California
Berkeley, California

Recent work by Walkley[10,11,12] on the $Mn - Mn^{++}$ and $Mn^{++} - MnO_2$ couples has done much to clarify the thermodynamics of the various oxidation states of manganese, and it now appears definite that cell measurements on the $Mn^{++} - MnO_2$ and $MnO_2 - MnO_4^-$ couples are reliable and reproducible when the manganese dioxide is in the form of pyrolusite, prepared by heating manganous nitrate. In order to confirm this and to bring the thermal data into line with the measured potentials, we have redetermined the heat of reaction,

$$MnO_4^- + 5/2\ H_2 + 3\ H^+ = Mn^{++} + 4\ H_2O \tag{1}$$
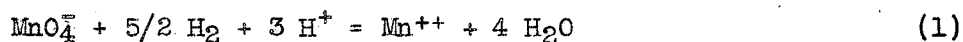
This heat and the entropy values have been employed to calculate the potential. As a summary the potential diagrams relating all of the oxidation states of manganese in uncomplexed solutions are given.

Apparatus and Materials. The calorimeter used in these measurements has been described previously.[2,6]

The reagents used were Bureau of Standards sample 40e sodium oxalate, Mallinckrodt analytical reagent grade potassium permanganate, G. F. Smith ferrous perchlorate and perchloric acid.

A stock solution approximately 3 molal in $Fe(ClO_4)_2$ and 0.5 molal in perchloric acid was prepared and standardized against a solution of $KMnO_4$ which in turn standardized against the primary standard $Na_2C_2O_4$.

All heats were measured at $25.0 \pm 0.2°C$ and are expressed in terms of the defined calorie.[7]

In order to use the heat given by Fontana[4] for the ferrous-ferric couple in 0.5 molal perchloric acid all heat determinations were carried out

in 0.5 molal perchloric acid, with reagent concentrations approximating
those of Fontana.

Heat of Dilution of the Ferrous Perchlorate Stock Solution. Weighed
portions of the ferrous perchlorate stock solution were sealed in glass bulbs
and broken into 0.500 molal perchloric acid in the calorimeter. Argon was
bubbled through the perchloric acid before final assembly of the calorimeter
in order to prevent air oxidation of ferrous ion. A titration of the diluted
ferrous perchlorate solution in the calorimeter at the conclusion of the
measurement showed no oxidation within the analytical accuracy.

The results of the calorimetric runs are shown in Table I. Using the
molality of the ferrous perchlorate stock solution, 2.834 m, it may be calcu-
lated that the heat of dilution is 1.88 k-cal/moles, that is for the reaction

$$Fe^{++} \text{ (2.834 molal in 0.5 molal } HClO_4) = Fe^{++} \text{ (0.016 molal in 0.5 molal } HClO_4) \quad (2)$$
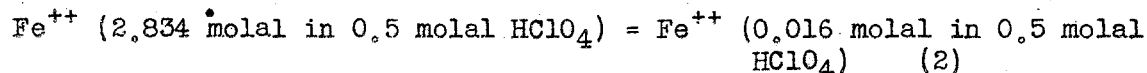
$\Delta H = -1.88$ k-cal/mole

Fontana[4] found for dilution from 1.937 molal to 0.025 molal $Fe(ClO_4)_2$ $\Delta H = -1.14$ k-cal/mole.

The heat of dilution from 0.025 to 0.016 should be small and virtually
all the difference in these two heats is undoubtedly due to the differing
initial ferrous perchlorate concentrations.

TABLE I

Heat of Dilution of Ferrous
Perchlorate Stock

Run	Weight of Stock	Heat evolved, cal.	Heat evolved/gm
1	9.3180 gm	27.38	2.94
2	9.8586	30.31	3.08
3	11.7678	35.16	2.99

Average 3.00 ± 0.05 calories
per gram of $Fe(ClO_4)_2$
stock solution.

Heat of Reaction of Permanganate Ion with Ferrous Ion. A sample of potassium permanganate was weighed out and delivered to the calorimeter and dissolved in water there. A weighed portion of 72 percent perchloric acid was then slowly added with stirring to make the solution 0.500 molal in perchloric acid. A weighed sample of the ferrous perchlorate stock solution was then introduced into a glass sample bulb and broken at an appropriate time in the calorimetric run.

It should be mentioned that the potassium permanganate which analysis showed to be 100.0 ± 0.1 percent pure was kept in an opaque vacuum dessicator over concentrated sulfuric acid throughout the course of the measurements. The ferrous perchlorate stock solution was kept under argon and showed less than 0.1 percent oxidation throughout the measurements.

The data obtained from the runs in which permanganate was reduced are given in Table II.

For the reaction

$$5\ Fe^{++} + 8\ H^{+} + MnO_4^{-} = 5\ Fe^{+++} + Mn^{++} + 4\ H_2O \qquad (3)$$
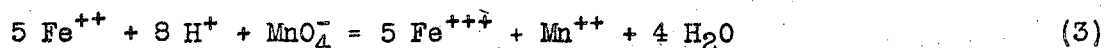
in 0.5 m $HClO_4$ we have obtained $\Delta H = -149.06$ kcal ± 0.12. Fontana[4] gave for the reaction

$$Fe^{++} + H^{+} = Fe^{+++} + 1/2\ H_2(g) \qquad (4)$$

in 0.5 m $HClO_4$, $\Delta H = +9.53 \pm 0.04$ kcal.

Hence for the reaction

$$5/2\ H_2(g) + 3\ H^{+} + MnO_4^{-} = Mn^{++} + 4\ H_2O \qquad (1)$$
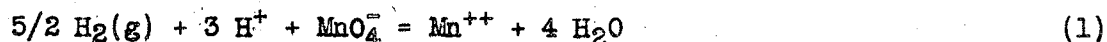
in 0.5 m $HClO_4$, $\Delta H = -196.71$ kcal. (± 0.23 kcal.)

According to the Bureau of Standards tables[7] the heat of dilution of $HClO_4 \cdot 100H_2O$, that is, approximately 0.5 m $HClO_4$, is less than 100 calories. Presumably the heat of dilution of permanganic acid in 0.5 m $HClO_4$ would also

be small. It remains for us to estimate the heat of dilution of manganous perchlorate in 0.5 m $HClO_4$. Unfortunately there is no reliable method of estimating this value, however, it seems reasonable that the heat of dilution of manganous perchlorate from 0.003 m to infinite dilution will also be small. We shall therefore take the heat of reaction (1) in pure water to be 196.71 ± 0.23 kcal.

The Mn - MnO_4^- Potential. The free energy of reaction (1) may now be calculated from the reaction heat and the entropies of the substances involved. For the entropies of MnO_4^-, H_2O and H_2 we shall use the Bureau of Standards[7] values; 45.4, 16.75 and 31.22 cal per deg. For the entropy of Mn^{++}, the Bureau of Standards gave -20, Walkley[10] gave -17.9 and Kapustinsky[5] -19.1. We shall use -19 ± 1.5 cal per deg. The ion entropies are referred to $S_{H^+}^O = 0$

$$\Delta S^O = S_{Mn^{++}}^O + 4 S_{H_2O}^O - 5/2 S_{H_2}^O - 3 S_{H^+}^O - S_{MnO_4^-}^O$$

$$= -19 + 67.00 \ 7 \ 78.05 - 0 - 45.4$$

$$= -75.45.$$

Then $\Delta F^O = \Delta H^O - T\Delta S^O$

$$= -196,710 - 298.16 \times (-75.45)$$

$$= -196,710 + 22500$$

$$= -174210 \text{ cal.}$$

This gives for the potential of the Mn^{++} - MnO_4^- couple in acid solution $E^O = -1.51$ volts.

We may now compare this value from thermal data with the measured potentials. Hutchinson[3] obtained the value 1.23 for the manganous-manganese dioxide (pyrolusite) couple in acid solution. Wadsly and Walkley[10] are in close agreement by cell measurements. These authors also discuss the value from thermal data, based upon the heat of formation of pyrolusite by Shomate[9]
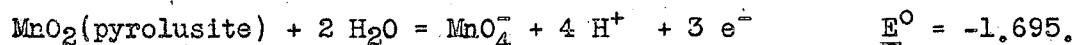
and write,

$$Mn^{++} + 2\ H_2O = MnO_2\ \text{(pyrolusite)} + 4\ H^+ + 2\ e^- \qquad \underline{E}^O = -1.229.$$
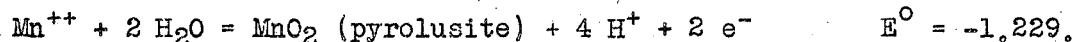
Andrews and Brown[1] found from direct cell measurements,

$$MnO_2\text{(pyrolusite)} + 4\ OH^- = MnO_4^- + 2\ H_2O + 3\ e^- \qquad \underline{E}^O = -0.588.$$
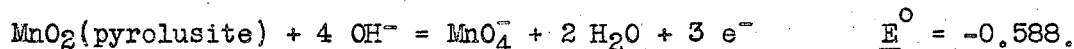
The corresponding value for acid solution is

$$MnO_2\text{(pyrolusite)} + 2\ H_2O = MnO_4^- + 4\ H^+ + 3\ e^- \qquad \underline{E}^O = -1.695.$$

Combining the two couples for the acid solutions, we find,

$$Mn^{++} + 4\ H_2O = MnO_4^- + 8\ H^+ + 5\ e^-$$
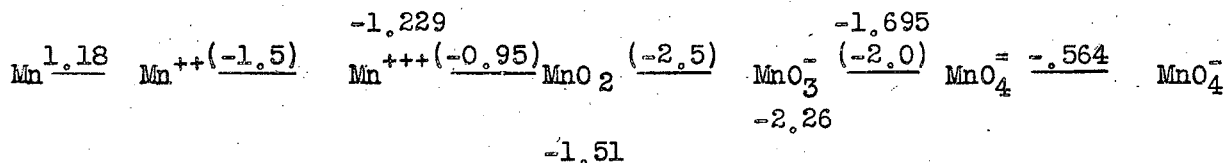
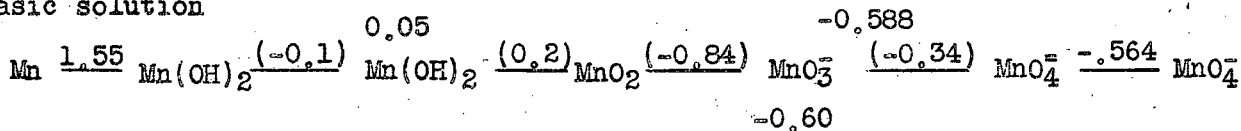$$\underline{E}^O = \frac{2\ x - 1.229 + 3\ x\ -1.695}{5} = -1.509.$$

The potential from cell measurements is thus in agreement with our value from thermal data.

Manganese Potential Diagram. As a summary of the various manganese potentials the following diagrams are given.

Acid solution

$$Mn \xrightarrow{1.18} Mn^{++} \xrightarrow{(-1.5)} Mn^{+++} \xrightarrow{-1.229} MnO_2 \xrightarrow{(-2.5)} MnO_3^- \xrightarrow{-1.695\ (-2.0)} MnO_4^= \xrightarrow{-.564} MnO_4^-$$

$$\overset{-2.26}{\underset{-1.51}{}}$$

Basic solution

$$Mn \xrightarrow{1.55} Mn(OH)_2 \xrightarrow{0.05\ (-0.1)} Mn(OH)_2 \xrightarrow{(0.2)} MnO_2 \xrightarrow{(-0.84)} MnO_3^- \xrightarrow{-0.588\ (-0.34)} MnO_4^= \xrightarrow{-.564} MnO_4^-$$

$$\underset{-0.60}{}$$

The $Mn - Mn^{++}$ potential is in approximate agreement with the work of Walkley[1]. The $Mn^{++} - Mn^{+++}$ and $Mn^{+++} - MnO_2$ are rough values (given in brackets) from the measurements of Grube and Huberich[4]. The values for the $MnO_2 - MnO_4^{--}$ and $MnO_4^{--} - MnO_4^-$ couples were obtained by recalculations of the equilibrium measurements of Schlesinger and Siems[8].

Values involving MnO_3^- are taken in agreement with the assumption that

the disproportionation into MnO_2 and MnO_4^{--} has a potential of about 0.5 volts. The couples in alkaline solution are calculated from the charge of potential with H^+ and values for the solubility products of $Mn(OH)_2$ and $Mn(OH)_3$.

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TABLE II

Heat of Reaction of Permanganate Ion

With Ferrous Ion

Run	Moles of KMnO$_4$	Wt of Fe(ClO$_4$)$_2$ Stock Solution	Observed Heat	Correction to Heat	Final Heat	H Kcal/mole
4	0.0031734	15.836 gm	520.00 cal	-47.52 cal	472.54	-148.90
5	0.0032682	15.577	532.54	-46.75	485.79	-149.10
6	0.0033304	15.825	644.29	-47.49	496.80	-149.17