Manganese Complexes with Bicarbonate and Sulfate in Natural Water

JOHN D. HEM
Geological Survey, U. S. Department of Interior, Denver 25, Colo.

The association constant for the dissolved species $MnHCO_3^+$ was experimentally determined to be 63. From this value and a published constant for the species $MNSO_4$ aq., a diagram was prepared showing per cent of dissolved manganese complexed in the presence of 10 to 10,000 p.p.m. bicarbonate and 1.0 to 10,000 p.p.m. sulfate. The rate of oxidation of Mn^{+2} in aerated water is greatly increased by increasing pH, and is retarded when SO_4^{-2} and HCO_3^- are present.

ALTHOUGH MANGANESE can exist at any oxidation state from 0 to +7, not all of these forms are stable within the range of pH and redox potential where water is stable, at a pressure of 1 atm. and a temperature of 25° C. In natural water the manganese species commonly encountered are at the +2, +3, or +4 oxidation states. At a pH above 13.5 and under oxidizing conditions, the +6 form may be dominant; but because natural water is unlikely to attain so high a pH, this form of manganese has little significance in natural-water environments.

Chemical relationships among the +2, +3, and +4 species of manganese have been studied in the laboratory and evaluated by techniques of chemical thermodynamics in recent research in the U. S. Geological Survey (*3*). This work also has considered the effects of the anions commonly present in natural water. Solid manganese minerals that are stable in the Eh-pH range of interest include oxides and hydroxides of all three oxidation states of the metal, and sulfides, and carbonate minerals in which the oxidation state of manganese is +2. The predominant dissolved species are Mn^{+2} ions and complexes of these ions with bicarbonate, sulfate, or hydroxide. The anion $HMnO_2^-$ can occur at high pH.

The purpose of this discussion is to evaluate the importance of the dissolved species $MnHCO_3^+$ and $MnSO_4$ aq. in natural water. In the compilation of stability constants prepared by Bjerrum, Schwarzenbach, and Sillen (*1*) mention is made of both complexes. For the equilibrium

$$Mn^{+2} + HCO_3^- \leftrightarrows MnHCO_3^+$$

the value for K is given as 3×10^3. For the equilibrium

$$Mn^{+2} + SO_4^{-2} \rightleftarrows MnSO_4 \text{ aq.}$$

the value for K is given as 1.9×10^2.

Manganese is a minor constituent in natural water and rarely is present in concentrations exceeding 1.8×10^{-5} molal, or 1.0 p.p.m. in terms of the commonly used units of water analysis. Complete complexing of these minor amounts of manganese would not significantly alter the relatively large activity of bicarbonate or sulfate ions in most water. Consequently, the proportion of manganese complexed can be simply estimated for each species from a single mass-law equation of the type:

$$\frac{[\text{Complexed Mn}]}{[\text{Uncomplexed Mn}]} = K\,[\text{Anion}]$$

According to the published constants, the manganese should be about 90% complexed in the presence of an activity of bicarbonate of 200 p.p.m. Laboratory studies of the solubility of manganese in dilute bicarbonate solutions, however, indicated the complexing effect was considerably below the predicted value. Accordingly, a new value for the association constant was determined from the solubility experiments.

The solubility experiments were made with analytical reagent grade manganese carbonate and demineralized distilled water, at 25° C. and 1 atm. pressure. Carbon dioxide gas was bubbled into this mixture for 16 hours. A constant pH was maintained for the last 8 hours of the experiment. Portions of the suspension were then partly degassed and transferred to tightly stoppered bottles where they were allowed to stand for periods ranging from 49 to 360 hours. The pH of the clear liquid was then measured, the manganese in solution determined by the periodate procedure, and the dissolved bicarbonate by potentiometric titration.

The manganese concentration included the amounts of Mn^{+2} and $MnHCO_3^+$, and the bicarbonate concentration included HCO_3^- and $MnHCO_3^+$. To determine the stability constant of the complex, a value for $[MnHCO_3^+]$ is needed, as well as values for $[Mn^{+2}]$ and $[HCO_3^-]$.

Equilibria that existed in the solutions included:

$$MnCO_3\,c + H^+ \leftrightarrows Mn^{+2} + HCO_3^- \qquad (1)$$

$$Mn^{+2} + HCO_3^- \rightleftarrows MnHCO_3^+ \qquad (2)$$

The equilibrium constant for Reaction 1 was calculated from free energy data published by Latimer (*4*) and by Garrels, Thompson, and Siever (*2*) to be 1.0.

Concentrations of bicarbonate and manganese ions in solution must be chemically equivalent; hence, each manganese ion must be accompanied by two bicarbonate ions. The activities of the complex and other ions can be conveniently computed by a method of successive approximation. As a first step, the complex was assumed to be absent. Activity coefficients were computed from the Mn^{+2} and HCO_3^- concentration data, and the Debye-Hückel law. Values obtained for $[Mn^{+2}]$ and $[HCO_3^-]$ were substituted in the mass-law expression of equilibrium 1

$$\frac{[HCO_3^-]\,[Mn^{+2}]}{[H^+]} = K$$

The value for K exceeded the 1.0 calculated for this constant from the free-energy data; therefore, the activities of Mn^{+2} and HCO_3^- were decreased by a suitable amount that was assigned to the form $MnHCO_3^+$, and the activity coefficients and activities of the uncomplexed species were recomputed. After a few repetitions a value for the activity of $MnHCO_3^+$ was obtained that fitted the analytical data to the equilibrium equation.

The computed values for $[MnHCO_3^+]$, $[Mn^{+2}]$, and $[HCO_3^-]$ substituted in equilibrium 2 gave values for K ranging from 45 to 80 and averaging 63; therefore, this average value was used as the association constant for the $MnHCO_3^+$ ion.

The value of 1.9×10^2 for the association constant of the $MnSO_4$ aqueous ion pair generally agrees with values for similar ion pairs of other transition metals. An activity of 510 p.p.m. (5.3×10^{-3} molal) of sulfate ions should be sufficient to complex half the small amount of manganese normally present in natural water. The association constant for the sulfate ion pair was not checked experimentally in this study.

Standard free energies of formation for the ion pairs computed from the equilibrium constants are

$$MnSO_4 \text{ aq.} = -234.8 \text{ kcal./mole}$$

$$MnHCO_3^- = -197.1\ (\pm 0.2) \text{ kcal./mole}$$

In all natural water some bicarbonate and sulfate ions are present, and their activities are frequently great enough to complex an appreciable proportion of the manganese. The species of complex that will predominate at any given activity of the two anions and the ratio of complexed to uncomplexed manganese in the solution can be readily calculated from thermodynamic data. Figure 1 is a graph that can be used to estimate the percentage of manganese complexed and the predominant form of complex in any solution where bicarbonate and sulfate activities are known.

The value of K for the equilibrium

$$MnSO_4\text{aq.} + HCO_3^- \rightleftarrows MnHCO_3^- + SO_4^{-2}$$

computed from free-energy data is 0.32. Therefore,

$$\frac{[MnHCO_3^-]}{[MnSO_4]} = \frac{0.32\,[HCO_3^-]}{[SO_4^{-2}]}$$

(quantities in brackets are molal activities). When the activities of the two complexes are equal, the relationship becomes $[SO_4^{-2}] = 0.32\ [HCO_3^-]$, which is the basis of the dashed line on Figure 1. Above and to the left of this line the bicarbonate complex predominates; below and to the right, the sulfate form predominates.

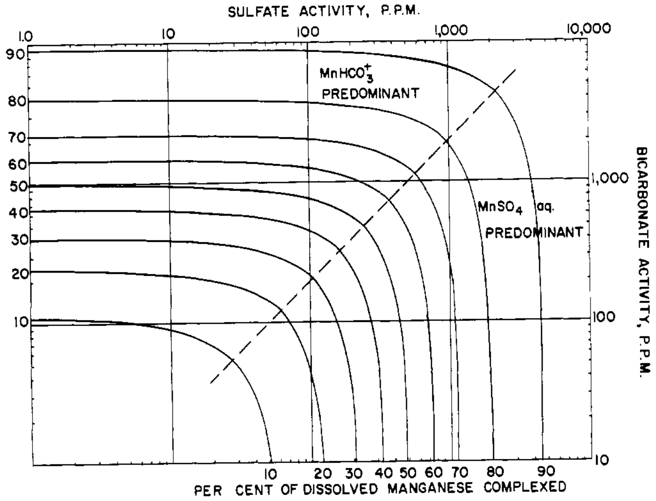

Figure 1. Percentage of total dissolved manganese present as complexes and predominant form of complex at different sulfate and bicarbonate activities

The curved lines on Figure 1 represent the percentage of the total activity of manganese complexed by combined activities of sulfate and bicarbonate. To locate the curves, lines representing different ratios of $[MnHCO_3^-]$ to $[MnSO^4]$ were drawn parallel to the dashed line representing the 1 to 1 ratio of complexes. On each of these lines a point was plotted corresponding to the activity of bicarbonate or sulfate required to maintain a given percentage of the total manganese activity in the form of complexes. Curves were fitted to these points.

For example, the point at which the activities of the two complexes are equal and the manganese complexed is 10% of the total manganese activity, can be calculated from the following relationships:

$$\frac{[MnSO_4]}{[MnHCO_3^-]} = 1$$

$$\frac{[MnSO_4] + [MnHCO_3^-]}{[Mn^{+2}]} = \frac{1}{9}$$

hence

$$\frac{[MnHCO_3^-]}{[Mn^{+2}]} = \frac{1}{18}$$

Substituting this value in the equation

$$\frac{[MnHCO_3^-]}{[Mn^{-2}]} = 63\,[HCO_3^-]$$

for the stability of the bicarbonate complex, gives a value of 8.81×10^{-4} molal for $[HCO_3^-]$ or 54 p.p.m. The intersection of 54 p.p.m. HCO_3^- with the 1 to 1 ratio diagonal represents one point on the 10% complexing curve. Other points on the curve were calculated similarly.

Figure 1 shows that bicarbonate and sulfate complexes could comprise a considerable part of the manganese in potable water. Concentration values reported in water analyses should be converted to activities using the Debye-Hückel equation for suitable accuracy in estimating the amount of complexing.

Oxidation of manganese from Mn^{-2} to Mn^{-3} or Mn^{-4}, accompanied by precipitation of oxides is important in removal of manganese from water, both in natural environments and in treatment of water supplies. Complexed forms of Mn^{-2} are more resistant to oxidation than "bare" Mn^{-2} ions. Complexing tends to increase amounts of unoxidized manganese remaining at equilibrium and lengthens the time required for equilibrium to be reached.

Some experimental results showing rates of Mn^{-2} oxidation and precipitation are given in Figure 2. Solutions of $MnCl_2$ which initially contained 2.0 mg. of manganese in 100 ml. of distilled water were maintained at a selected constant pH by additions of KOH. Oxygen from the air was present in excess. Portions taken for analysis were filtered through a plastic membrane filter having pores 0.45 of a micron in diameter.

The reaction rate is highly pH-sensitive. At pH 9.0 the reaction half time is about 1½ minutes and at pH 8.5, about 30 minutes. The reaction mechanisms were not closely studied but in general the relation between log Mn concentration and time was linear. The experiment was repeated using a solution of sodium sulfate containing 2,000 p.p.m. SO_4^{-2} instead of distilled water. Results at pH 9.0 are shown near the top of Figure 2. The rate at which manganese was oxidized and precipitated was nearly constant for the first 50 minutes, but increased thereafter. The increasing rate may have resulted from the autocatalytic effect of manganese oxide.

The activity of SO_4^{-2} in the solution was about 900 p.p.m. According to Figure 1 about two thirds of the manganese present was in aqueous $MnSO_4$. The complex probably decreased the rate by decreasing the availability of Mn^{+2}.

In another series of experiments 2.0 mg. of Mn^{-2} was added to 100 ml. of distilled water containing 100 p.p.m. HCO_3^- and an equivalent amount of Na^+. The pH of these solutions was then raised to a selected level and maintained there by additions of sodium hydroxide solu-

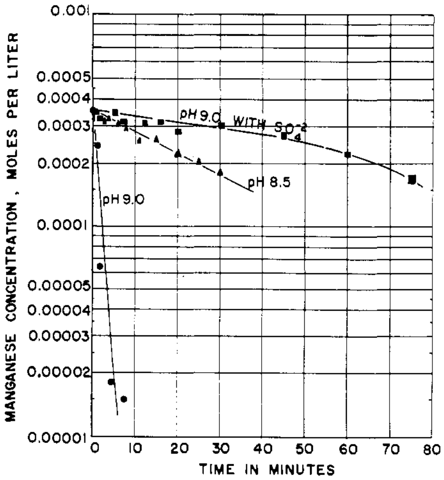

Figure 2. Rate at which manganese was oxidized at pH 8.5 and 9.0 in the absence of sulfate and at pH 9.0 with a sulfate concentration of 2,000 p.p.m.

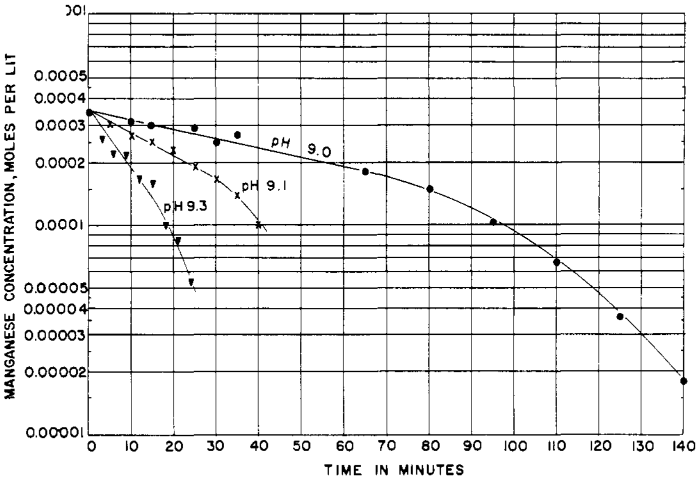

Figure 3. Rate at which manganese was oxidized at three pH levels in the presence of 100 p.p.m. of bicarbonate

tion. Aliquots were removed and filtered as before to determine the change in dissolved manganese with time. The results of runs at pH 9.0, 9.1, and 9.3 are shown in Figure 3. All three of the sets of data show that a constant rate of oxidation and precipitation of manganese is maintained at first, but the rate increases during the latter part of the experiment.

The effect of HCO_3^- ions on the rate of oxidation is greater than would be expected from the stability of the $MnHCO_3^+$ ion. Possibly a different and stronger complex may form at pH 9.0, or the availability of OH^-, which speeds the oxidation, may be decreased by the carbonate species in solution.

The effects of both complexes considered here may be significant in water-supply chemistry as well as in other aspects of natural-water chemistry. A clear understanding of the chemical behavior of any dissolved element can be attained only by considering all species of the element present in the solution.

LITERATURE CITED

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RECEIVED for review May 21, 1962. Accepted August 6, 1962. Division of Water and Waste Chemistry, 141st Meeting, ACS, Washington, D. C. March 1962.