

Chemical Equilibria and Rates of Manganese Oxidation

By JOHN D. HEM

CHEMISTRY OF MANGANESE IN NATURAL WATER

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UNITED STATES DEPARTMENT OF THE INTERIOR

STEWART L. UDALL, *Secretary*

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Thomas B. Nolan, *Director*

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CHEMISTRY OF MANGANESE IN NATURAL WATER

CHEMICAL EQUILIBRIA AND RATES OF MANGANESE OXIDATION

By JOHN D. HEM

ABSTRACT

The relationships between manganese in solution, Eh, pH, and the activities of bicarbonate and sulfate ions are shown by means of seven stability-field diagrams. The behavior of manganese in laboratory experiments is in general agreement with predictions of the diagrams. In distilled water, with an Eh near 0.55 volts and a pH of 7.0, manganese has a solubility of about 1.0 ppm (parts per million). An increase in pH or in Eh tends to lower the solubility.

Bicarbonate species in equilibrium with manganese carbonate may control manganese solubility in some systems. Increased bicarbonate activity decreases manganese solubility. Relationships between manganese and sulfate activities are related to solution of manganese sulfide with oxidation of the sulfur.

Manganese forms soluble complexes with bicarbonate and sulfate. The association constant for MnHCO_3^+ ion was determined to be 63. The solubility of manganese in natural water, especially that which contains large amounts of bicarbonate or sulfate, is influenced by complexing. In a solution where the total dissolved manganese is 1.0 ppm, the activity of sulfate is 250 ppm, and bicarbonate activity is 470 ppm, half the manganese present will be in the complexes.

The rate at which divalent manganese is oxidized and precipitated from aerated solutions is sharply increased by increasing the pH. The rate is diminished when sulfate and bicarbonate ions are present. Experimental data suggest that the reaction may be first order with respect to manganese concentration initially, but the rate increases as the reaction proceeds, probably because of autocatalysis.

Manganese coprecipitates with ferric hydroxide when the pH is greater than 6.7.

AIMS AND ORGANIZATION OF STUDY

Although manganese is a minor constituent of natural water, even small concentrations of the element constitute an undesirable impurity in water to be used for domestic and for many industrial purposes. The U.S. Geological Survey is conducting research in the chemical behavior of manganese and other hydrosoluble metals. These elements are readily soluble under some of the chemical conditions common to natural water, but under some others, also common to natural water, they form oxides and hydroxides of very low solubility.

The research work includes systematic description and evaluation of the factors affecting solubility of manganese under conditions of chemical equilibrium and study of some factors affecting reaction rates. The effects of macrobiota and microbiota are also considered, together with factors more directly related to inorganic chemical behavior. This report is the first of a series describing the results of research on the chemistry of manganese.

The research work described in this report was done in laboratories of the U.S. Geological Survey in Denver, Colo. The author was assisted in the laboratory work by M. J. Fishman. Helpful suggestions in the course of the study and in review of the manuscript were furnished by colleagues of the author in the Geological Survey and by Professor R. M. Garrels, Department of Geological Sciences, Harvard University.

OCCURRENCE AND CHEMICAL PROPERTIES OF MANGANESE

The element manganese is number 25 in the periodic table. It is classified as a transition element and displays some chemical characteristics, such as multiple valency, that are typical of that group of elements. Only one isotope of the element, Mn^{55} , exists naturally, although nuclides of higher and lower mass number, all radioactive, have been produced artificially. Manganese is located adjacent to iron in the periodic table, and the two elements have some chemical resemblances. The two elements are often considered together, particularly in the technology of water supply and treatment, because they cause similar problems and both may need to be removed. Because the chemistry of manganese is different from that of iron in several important respects, manganese is much more difficult to remove from water than iron.

It is generally agreed that the amount of manganese present in the rocks of the earth's crust averages about 0.10 percent. This contrasts with a concentration of nearly 5.0 percent for iron. Thus, the abundance data suggest that manganese should be much less common in solution in natural water than is iron, and, in general, this expectation is realized. In many places the rarity or absence of manganese-containing minerals may prevent saturation of the natural water. In such places the solubility and rates of solution of the minerals are not the only controls on the concentration of manganese in the water. However, manganese-bearing minerals are common in sedimentary rocks and soils. Manganese in igneous rocks commonly occurs as a minor component in many minerals, such as the pyroxenes, olivines, and amphiboles, but independent manganese minerals are scarce.

Combined or ionic manganese can occur at oxidation levels from +1 to +7. In natural environments, however, some of these oxida-

tion states are not likely to occur. In the presence of water, under conditions to be expected at or near the surface of the earth, only the +2, +3, +4, and +6 states are stable. Species of manganese in the +7 state (permanganate, MnO_4^-) are commonly utilized in the laboratory, and solutions of permanganate have sufficient stability to be used in oxidation-reduction titrations. The oxidizing power of permanganate, however, is great enough to release oxygen from water, although ordinarily the reaction is very slow.

The principal common minerals of manganese are the oxides and hydroxy-oxides, such as the minerals pyrolusite (MnO_2) and psilomelane [$\text{BaMn}^{+2}\text{Mn}^{+4}_8\text{O}_{16}(\text{OH})_4$]. Mixtures of pyrolusite with manganite [$\text{MnO}(\text{OH})$], braunite [$(\text{Mn},\text{Si})_2\text{O}_3$], hausmanite [Mn_3O_4], and psilomelane are common in nearsurface environments. Mixtures whose exact mineral composition may not be known are termed "rad," a generic name for earthy mixtures. The adsorptive capacity of manganese oxy-hydroxide precipitates has been credited for the complex assemblage of impurities often found in earthy masses of manganese minerals. Less common minerals are the more reduced pyrochroite [$\text{Mn}(\text{OH})_2$] and manganosite (MnO).

As is common for the transition elements, some of the compounds of manganese listed above appear to be mixtures of two formal oxidation states or valences.

Rhodochrosite, the manganese carbonate, occurs in some ore deposits and is an impurity in some carbonate rocks. The sulfide alabandite (MnS) is relatively scarce.

Data on the speed of oxidation-reduction reactions involving the +2, +3, and +4 forms of manganese are very sparse, and nothing useful was found in published literature. The present study shows that these reactions are slower than similar ones involving iron, which Stumm and Lee (1961) found were generally rapid at the pH levels of most natural water. Nevertheless, the oxidation of Mn^{+2} is rapid enough under favorable conditions, especially when increased by the catalytic action of micro-organisms, to reach equilibrium in natural systems. Therefore, an equilibrium treatment of manganese systems likely to be found in natural water is logical, particularly for the conditions relating to solution and solubility, and has been chosen as a logical approach here. However, it should be recognized that the representation of solid phases has been simplified to the point where that part of the treatment may not approach natural conditions closely.

NATURE AND SIGNIFICANCE OF STABILITY-FIELD DIAGRAMS

The stability-field, or Eh-pH, diagram is a graphical means of showing the conditions of redox potential and hydrogen-ion concentra-

tion that are compatible with specified dissolved ions and solid species of an element at chemical equilibrium in the presence of water. The Eh-pH graph apparently was first utilized in Europe by Pourbaix (1949). In its original form, the diagram was used principally in studies of the factors involved in corrosion of metals. Stability-field diagrams, however, have proved to be useful for representing in clear and concise form the important features of the chemical behavior of many of the elements under the conditions that prevail in natural systems. The literature contains numerous examples of the use of these diagrams in studies of the origin of ore deposits and in other geologic applications, and the diagrams have been used also in studies relating to oceanography and limnology. Garrels (1960) has described methods of preparing and using Eh-pH diagrams. The principal features of the chemistry of iron have been shown by such diagrams (Hem and Cropper, 1959); and because manganese is strongly affected in its behavior in natural environments, both by oxidation and reduction and by hydrogen-ion concentration, stability-field diagrams have been used in this discussion.

In preparing the diagrams, certain basic assumptions are made and should be kept in mind when making interpretations. The fundamental equations used are those dealing with a state of chemical equilibrium among the dissolved and solid-phase species. If all the chemical reactions involved are relatively rapid and thus reach equilibrium quickly, no uncertainty is introduced by assuming the existence of equilibrium. If reactions are slow, forms of an element may exist under conditions that are chemically unfavorable for long periods of time. Where very long time intervals are involved, as in some geologic systems, a slow reaction may tend to reach equilibrium, but the reaction time in most natural-water systems near the earth's surface is short in the geologic sense.

However, even though it is uncertain that all the manganese species considered could be logically expected to reach chemical equilibrium in natural water, the stability-field diagram is still useful to indicate limiting conditions. Laboratory experiments described in this report and field observations can be used as aids to determine the practical usefulness of theoretical calculations.

The diagrams are prepared for a pressure of 1 atmosphere and a temperature of 25°C and are strictly applicable only under these conditions, although pressures of a few atmospheres and temperatures of 10° or 15° above or below 25°C do not introduce serious error. The natural systems that are of interest in the study of the chemistry of manganese in natural water generally will involve more complex compounds than are dealt with here. The aqueous phase will usually

contain other constituents in addition to the manganese species. The systems are affected to a lesser degree by departures from standard conditions of temperature and pressure. In general, the effects of minor deviations in composition of the substances involved in natural systems from the composition assumed in the diagrams cannot be evaluated. Standard computations of chemical thermodynamics can provide results applicable to any temperature or pressure that is likely to be found.

The manganese concentrations indicated in that part of the stability-field diagram where dissolved species predominate are the effective, or thermodynamic, concentrations (activities) rather than the concentrations that would be measured by chemical analysis. In extremely dilute solutions, these thermodynamic concentrations are almost equal to the actual concentrations; but as the amount of dissolved material increases, the freedom of charged ions to move in the solution is decreased. As a result the effectiveness of a given concentration of ions to participate in reactions decreases as total concentration increases.

The measured concentrations reported in chemical analysis may be converted to thermodynamic concentrations by means of a computed activity coefficient. Techniques for performing this computation are given in the literature (Klotz, 1950), and adaptations for natural waters were described by the writer (Hem, 1961). For an ion with a dual charge, such as Mn^{+2} , the activity will be 85 to 90 percent of the measured concentration when the dissolved-solids concentration of the water in which the ion occurs is about 50 ppm. In water containing from 3,000 to 5,000 ppm (parts per million) of dissolved solids, the activities may be less than half of the measured concentrations.

When using stability-field diagrams to interpret water analyses, the analytical data must be converted to activities. For water that is very highly mineralized, accurate conversion to activities may not be possible.

CHEMICAL-EQUILIBRIUM COMPUTATIONS

The stability-field diagram utilizes the following basic relationships of chemical thermodynamics:

$$\Delta F^\circ = -RT \ln K \quad (1)$$

$$E^\circ = \frac{-\Delta F^\circ}{nf} \quad (2)$$

$$E_h = E^\circ + \frac{RT}{nf} \ln \frac{a_{\text{ox.}}}{a_{\text{red.}}} \quad (3)$$

Symbols used in the equations are:

ΔF° = standard free-energy change in chemical reaction, in kilogram-calories

R = universal gas constant (1.987 calories per degree mole or 8.314 joules per degree mole)

T = temperature, in degrees Kelvin

\ln = logarithm to base "e"

n = number of electrons appearing in the redox equation

f = Faraday constant (23,060 calories per volt or 96,484 coulombs per gram equivalent)

E° = standard potential, in volts

Eh = redox potential

$\frac{a \text{ ox.}}{a \text{ red.}}$ = activities of oxidized and reduced species as expressed in mass action equations.

If the system is more oxidized than the hydrogen half-cell (partial pressure of $H_2 < 1$ atmosphere), the potential of the half-cell will be taken as positive. This is the conventional means of representing such values in geochemical literature. The chemical reactions that the equations are used to evaluate are written here as reductions—that is, the representation of electrons in the equation is on the left-hand side.

The sign conventions used in Eh calculations are chosen arbitrarily. If chemical reactions are written as oxidations and if systems more oxidized than the hydrogen half-cell are given a positive sign, the negative sign in equation (2) must be changed to positive.

Table 1 contains published values for the standard free energies of formation of manganese species and other species of importance in this discussion. The most recent compilation of such data for manganese species is that of Mah (1960). Supplementary data are taken mostly from the compilation of Latimer (1952). Several values in the table were calculated from information published in other sources, such as the compilation of stability constants of Bjerrum, Schwarzenbach, and Sillén (1958). Free-energy values may be obtained from data of this kind from the appropriate chemical equation and the relationships

$$\Delta F^\circ = -RT \ln K$$

and

$$\Delta F^\circ = \Sigma \Delta F^\circ \text{ products} - \Sigma \Delta F^\circ \text{ reactants}$$

when the standard free energies of formation of all the products and reactants, except one, are known. Some writers refer to the net change in standard free energy occurring in a chemical reaction as "standard reaction potential".

TABLE 1.—Free energy of formation (25° C) of gaseous (g), crystalline (c), liquid (l), and dissolved (aq) substances considered in stability-field diagrams

Species	ΔF° (kg-cal)	Source of data
Mn ²⁺ (aq) -----	-54.4	Latimer (1952, p. 235).
MnOH ⁺ (aq) -----	¹ -96.6	Chaberek, Courtney, and Martell (1952).
Mn(OH) ₂ (c) -----	-146.9	Latimer (1952, p. 235).
HMnO ₂ ⁻ (aq) -----	-120.9	Do.
MnCO ₃ (c) (rhodochrosite) -	-195.4	Mah (1960), Latimer (1952, p. 235).
MnCO ₃ (c) (precipitated) -	-194.7	Garrels, Thompson, and Siever (1960).
MnS (c) -----	-50.55	Mah (1960).
MnO (c) -----	-86.75	Do.
MnSiO ₃ (c) -----	-289.0	Do.
Mn ₂ SiO ₄ (c) -----	-381.95	Do.
MnHCO ₃ ⁺ (aq) -----	-197.1	Determined in this study.
MnSO ₄ (aq) -----	-234.8	James (1947); Bjerrum, Schwarzenbach, and Sillén (1958, p. 82).
Mn ₃ O ₄ (c) -----	-305.85	Mah (1960).
Mn ³⁺ (aq) -----	-19.6	Latimer (1952, p. 235).
Mn(OH) ₃ (c) -----	-181.	Do.
Mn ₂ O ₃ (c) -----	-209.85	Mah (1960).
MnO ₂ (c) -----	-111.3	Do.
MnO ₄ ⁻² (aq) -----	-120.4	Latimer (1952, p. 235).
H ₂ O (l) -----	-56.69	Latimer (1952, p. 39).
OH ⁻ (aq) -----	-37.595	Do.
H ₂ CO ₃ (aq) -----	-149.00	Latimer (1952, p. 128).
HCO ₃ ⁻ (aq) -----	-140.31	Do.
CO ₃ ⁻² (aq) -----	-126.22	Do.
H ₂ S (aq) -----	-6.54	Latimer (1952, p. 72).
HS ⁻ (aq) -----	3.01	Do.
HSO ₄ ⁻ (aq) -----	-179.94	Do.
SO ₄ ⁻² (aq) -----	-177.34	Do.
CO ₂ (g) -----	-94.26	Latimer (1952, p. 128).
S (c) -----	0.0	Latimer (1952, p. 72).

¹ Determined at 30 °C.

The standard free energy of formation of the complex ion MnHCO₃⁺ was determined experimentally in this research study.

Table 2 is a compilation of some of the equilibrium constants that are utilized extensively in this report. Values shown in table 2 as "calculated" were computed from free-energy values in table 1. The values ascribed to other authors were taken directly from their quoted values. Probably, because of rounding off, some of these differ slightly from the results obtained by calculation from the free energies in table 1.

The distribution of manganese species in stability-field diagrams in this report is given only for conditions under which water is stable. The redox potential at which water is oxidized with the liberation of gaseous oxygen is 1.23 v (volts) at a pH of 0. At a pH of 14, the Eh for this reaction is just over 0.4 v. Water may be reduced to liberate gaseous hydrogen at Eh values of less than 0 v at a pH of 0 and at Eh values of less than -0.82 v at a pH of 14. Although it is usually assumed that pH-Eh conditions beyond the water-

TABLE 2.—*Equilibrium constants utilized in constructing stability-field diagrams*

Reaction	Equilibrium constant	Source of data
$\text{Mn}(\text{OH})_2 \text{ (c)} + \text{H}^+ = \text{MnOH}^+ + \text{H}_2\text{O}$ -----	4.9×10^4 -----	Calculated.
$\text{MnOH}^+ + \text{H}^+ = \text{Mn}^{+2} + \text{H}_2\text{O}$ -----	4.2×10^{10} -----	Chaberek, Courtney, and Ma-tell (1952).
$\text{Mn}(\text{OH})_2 \text{ (c)} = \text{HMnO}_2^- + \text{H}^+$ -----	8.7×10^{-30} -----	Calculated.
$\text{Mn}^{+2} + \text{HCO}_3^- = \text{MnHCO}_3^+$ -----	63-----	Determined in this study.
$\text{Mn}^{+2} + \text{SO}_4^{2-} = \text{MnSO}_4(\text{aq})$ -----	1.9×10^2 -----	James, J. C. (1947) in Bjerrum, Schwarzenbach, and Sillen (1958) p. 82.
$\text{MnS} + 2\text{H}^+ = \text{H}_2\text{S} + \text{Mn}^{+2}$ -----	4.14×10^7 -----	Calculated.
$\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$ -----	4.16×10^{-7} -----	Latimer (1952, p. 135).
$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$ -----	4.84×10^{-11} -----	D.
$\text{H}_2\text{S} = \text{H}^+ + \text{HS}^-$ -----	1.1×10^{-7} -----	Latimer (1952, p. 71).
$\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$ -----	1.26×10^{-3} -----	Latimer (1952, p. 74).
$\text{MnCO}_3 \text{ (c) (rhodochrosite)} + 2\text{H}_2\text{O} = \text{Mn}(\text{OH})_2 \text{ (c)} + 2\text{H}^+ + \text{CO}_3^{2-}$ -----	7.4×10^{-27} -----	Calculated.
$\text{MnCO}_3 \text{ c (ppt)} + 2\text{H}_2\text{O} = \text{Mn}(\text{OH})_2 \text{ (c)} + 2\text{H}^+ + \text{CO}_3^{2-}$ -----	2.3×10^{-26} -----	D.
$\text{MnHCO}_3^+ + \text{H}^+ = \text{Mn}^{+2} + \text{H}_2\text{CO}_3(\text{aq})$ -----	4.2×10^4 -----	D.

stability boundaries are not likely to occur in nature, an Eh considerably above or below these limits is necessary in order to cause water to decompose at a readily observable rate. Consequently, the area outside the water-stability boundaries may have some practical significance, especially in laboratory work. For present purposes, however, only the area within which water is stable will be considered.

Figure 1 shows the fields of stability for 4 solid phases of manganese and the fields of dominance of 3 dissolved species of manganese. Interfering anions and cations are absent. This is about the simplest representation that can be made for a manganese system that includes enough variables to approach actual conditions in laboratory solutions. The four solids having fields of stability in the figure are MnO_2 , Mn_2O_3 , Mn_3O_4 , and $\text{Mn}(\text{OH})_2$. The symbol (c) on the diagram indicates crystalline (solid) material. Free-energy values given in table 1 show that MnO would be changed to $\text{Mn}(\text{OH})_2$ and that $\text{Mn}(\text{OH})_3$ would dehydrate even in contact with water; consequently, such forms do not appear on the diagram. The compound $\text{Mn}(\text{OH})_4$, has been mentioned in the literature but proof of its existence is lacking.

The solid lines represent the positions of the boundaries of the stability fields of solids, when the effective concentration of dissolved manganese is 0.01 ppm (1.8×10^{-7} molal). The dissolved species considered are Mn^{+2} , MnOH^+ , and the anionic form HMnO_2^- . All these are varieties of divalent manganese. Within the stability limits of water, Mn^{+3} (aq) is less abundant than Mn^{+2} and is not considered. The line along which $\text{Mn}^{+3} = \text{Mn}^{+2}$ is above 1.23 v at a pH of 0. Also, with one minor exception, the highly oxidized anionic species are stable only outside this area. Therefore Mn^{+7} (as in permanganate) is not considered. Near a pH of 14 and an Eh of +0.40, the stability boundary between the manganate ion, in which

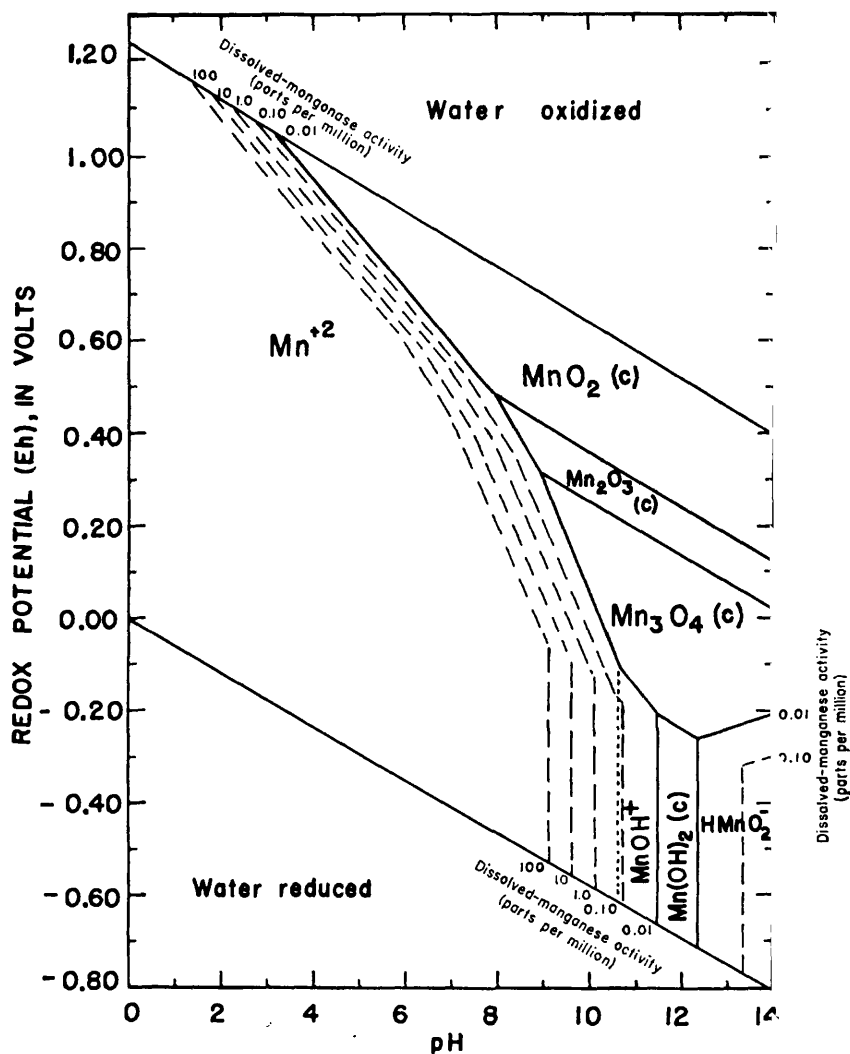


FIGURE 1.—Stability fields of manganese species in aqueous solution, free of bicarbonate and sulfate ions. Total dissolved-manganese activity ranges from 0.01 to 100 ppm.

the manganese is hexavalent, and MnO_2 (c) intersects the water-stability boundary. However, the area of stability of manganate is very small and lies in a region that never exists in nature. Hence, the manganate species have been omitted from the diagrams. The area in which the aqueous hydroxide complex is the dominant dissolved species is separated from the Mn^{+2} (aq) region by a dotted line. Dashed lines represent the positions of the stability-field boundaries of the solids when dissolved Mn^{+2} activity is 0.10, 1.0, 10,

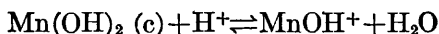
and 100 ppm. These dashed lines are, in effect, solubility "contours" for manganese in the system described as functions of pH and Eh.

Activities of dissolved manganese and of anions are given in parts per million, because this unit is the most widely used in water chemistry. However, the calculations require that reactant activities be expressed in moles. Molar concentrations (moles per liter) are related to molal concentrations (moles per kilogram of solution) in the same way as milligrams per liter are related to parts per million. In dilute solutions, such as the ones considered here, the difference between molal and molar quantities is insignificant.

LOCATION OF STABILITY BOUNDARIES

The chemical concepts and calculations used in determining the positions of the boundaries in figure 1 are similar to the procedures described by Garrels (1960) and previously used by the writer (Hem and Cropper, 1959, Hem, 1960a) in making similar diagrams for iron. The steps in preparing figure 1 are as follows: Boundaries for the field of stability for water are drawn first. Within the water-stability area, species whose stability fields are separated by vertical boundaries (no reduction or oxidation involved) are those of Mn^{+2} and represent a simple starting point.

The only solid Mn^{+2} variety is $\text{Mn}(\text{OH})_2$. This hydroxide is amphoteric. As pH decreases, the equilibrium



shifts to the right. The equilibrium constant (table 2) is 4.9×10^4 . We may write

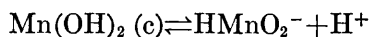
$$\frac{[\text{MnOH}^+][\text{H}_2\text{O}]}{[\text{Mn}(\text{OH})_2][\text{H}^+]} = 4.9 \times 10^4.$$

The activity terms, which are expressed in moles per liter, or in moles per kilogram of dilute solutions, are those enclosed in brackets. If the activity of dissolved manganese, here almost all in the MnOH^+ form, is taken as 1.8×10^{-7} molal (0.01 ppm) and the activities of water and of the solid $\text{Mn}(\text{OH})_2$ are taken as unity (by definition), the equation may be solved for $[\text{H}^+]$.

$$[\text{H}^+] = \frac{1.8 \times 10^{-7}}{4.9 \times 10^4} = 3.7 \times 10^{-12}.$$

The negative log (pH) of this value is 11.4, hence the boundary between $\text{Mn}(\text{OH})_2 (c)$ and MnOH^+ is drawn vertically at this pH value.

At higher pH the equilibrium



increases in importance. The equilibrium constant for this reaction (table 2) is 8.7×10^{-20} . This leads to the equation

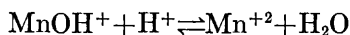
$$\frac{[\text{HMnO}_2^-] [\text{H}^+]}{[\text{Mn}(\text{OH})_2]} = 8.7 \times 10^{-20}.$$

Here again the activity of $\text{Mn}(\text{OH})_2 (\text{c})$ is taken as unity, and the activity of the manganite ion as 1.8×10^{-7} molal. Thus

$$[\text{H}^+] = \frac{8.7 \times 10^{-20}}{1.8 \times 10^{-7}} = 4.8 \times 10^{-13},$$

and the equivalent pH is 12.3. This represents the high pH boundary of the $\text{Mn}(\text{OH})_2 (\text{c})$ stability field.

The MnOH^+ complex ion is further dissociated into Mn^{+2} and OH^- as the pH decreases. The dissociation may be written



for which the equilibrium constant is 4.2×10^{10} (table 2). This leads to the relationship

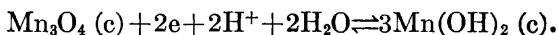
$$\frac{[\text{Mn}^{+2}] [\text{H}_2\text{O}]}{[\text{MnOH}^+] [\text{H}^+]} = 4.2 \times 10^{10}.$$

The activity of water may again be assigned a value of 1. At the boundary between the Mn^{+2} and the MnOH^+ fields, the two species will be at equal activity. The equation then simplifies to

$$[\text{H}^+] = \frac{1}{4.2 \times 10^{10}} = 2.4 \times 10^{-11},$$

which is equivalent to pH 10.6. It should be noted that this boundary is not dependent on manganese concentration. To prevent it from being confused with the solid lines separating solid from aqueous species in figure 1, the boundary is represented by a dotted line.

The other field boundaries on figure 1 are influenced by both pH and Eh. The solids considered have already been enumerated. The equilibrium between manganous hydroxide and the mixed oxide Mn_3O_4 is (written as a reduction):



The mixed oxide can be considered as containing 1 unit of Mn^{+2} and 2 of Mn^{+3} . The two Mn^{+3} atoms are reduced to the Mn^{+2} state, using two unit negative charges, as represented by "e" in the equilibrium. The net standard free-energy change in this equilibrium, ΔF^0 net, can be determined from data in table 1:

$$\Delta F^0 \text{ net} = 3\Delta F^0_{\text{Mn(OH)}_2 \text{ (c)}} - \Delta F^0_{\text{Mn}_3\text{O}_4 \text{ (c)}} - 2\Delta F^0_{\text{H}_2\text{O}} \quad (1)$$

in which the standard free energy of H^+ is zero.

$$\begin{aligned} \Delta F^0 \text{ net} &= 3(-146.9) - (-305.85) - 2(-56.69) \\ &= -440.7 + 419.23 = -21.47 \text{ kg-cal.} \end{aligned}$$

The standard redox potential E^0 for the equilibrium can now be determined from the relation

$$\begin{aligned} E^0 &= -\frac{\Delta F^0}{nf} = \frac{21.47}{2(23.06)} \\ E^0 &= 0.466 \text{ v.} \end{aligned}$$

The value for the oxidation potential of the system when the participating substances are not at unit activity can be computed from the Nernst equation. For the above reaction, the Nernst equation with numerical values entered for constants and using base-10 logs takes the form

$$\text{Eh} = 0.466 + \frac{0.0592}{2} \log \frac{[\text{Mn}_3\text{O}_4][\text{H}_2\text{O}]^2[\text{H}^+]^2}{[\text{Mn(OH)}_2]^3}.$$

The activities of solids and of water are again unity, and the equation may then be simplified to

$$\begin{aligned} \text{Eh} &= 0.466 + \frac{0.0592}{2} \log [\text{H}]^2, \text{ or} \\ \text{Eh} &= 0.466 - 0.0592 \text{ pH.} \end{aligned}$$

The vertical boundaries already drawn in figure 1 determine the lateral extent of the Mn(OH)_2 field. At a pH of 12.3, the Eh becomes -0.26 v, and at a pH of 11.4 the Eh value is -0.22 v. A line connecting these points is then drawn to define the boundary between Mn(OH)_2 (c) and Mn_3O_4 (c).

Similar calculations are based on the equilibria $3\text{Mn}_2\text{O}_3 \text{ (c)} + 2\text{e} + 2\text{H}^+ \rightleftharpoons 2\text{Mn}_3\text{O}_4 \text{ (c)} + \text{H}_2\text{O}$, where $E^0 = 0.842$ v, and $2\text{MnO}_2 \text{ (c)} + 2\text{e} + 2\text{H}^+ \rightleftharpoons \text{Mn}_2\text{O}_3 \text{ (c)} + \text{H}_2\text{O}$, where $E^0 = 0.953$ v, to establish the boundary between Mn_3O_4 (c) and Mn_2O_3 (c) and between Mn_2O_3 (c) and MnO_2 (c).

Boundaries between dissolved and solid species involve the following equilibria:



and



Values for the standard potentials are computed from net standard free-energy change. The value for Eh for the first of these equilibria then is

$$\text{Eh} = 0.881 + \frac{0.0592}{2} \log \frac{[\text{H}]^5}{[\text{MnOH}^+]^3}.$$

The activity of dissolved Mn species along the boundary is 1.8×10^{-7} molal. Hence,

$$\text{Eh} = 0.881 + 0.0888(6.74) - 0.148 \text{ pH}.$$

A similar procedure is followed for each of the equilibria.

If the activities of dissolved manganese species are increased, the stability fields of solids become larger. The dashed lines in figure 1 represent the positions of the solid-aqueous species boundaries when dissolved manganese activity is increased successively to 0.10, 1.0, 10, and 100 ppm. These dashed lines were plotted from calculations similar to those made for the 0.01 ppm boundaries, but the larger values for manganese activity were used. Boundaries between solids are not affected by the concentrations of dissolved manganese.

In general, no more than one form of dissolved manganese needs to be considered in the fields of dominance portrayed. In figure 1, however, near the $\text{MnOH}^+ - \text{Mn}^{+2}$ boundary, a more exact position of the dashed line representing 0.10 ppm total dissolved manganese can be made if presence of both Mn^{+2} and MnOH^+ is assumed. The equilibria that need to be considered in calculating H^+ for this dissolved manganese activity are



Equilibrium constants from table 2, assuming water and solids to have unit activity, lead to the equations

$$\frac{[\text{MnOH}^+]}{[\text{H}^+]} = 5.1 \times 10^2 \text{ and } \frac{[\text{Mn}^{+2}]}{[\text{MnOH}^+][\text{H}^+]} = 4.2 \times 10^{10}.$$

Also, because the total manganese in solution is fixed at 0.10 ppm.

$$[\text{Mn}^{+2}] + [\text{MnOH}^+] = 1.8 \times 10^{-6} \text{ (or } 1.8 \times 10^{-6} \text{ molal).}$$

These three equations can be solved simultaneously to give a value of 1.9×10^{-11} for $[\text{H}^+]$.

Calculations for activity of dissolved manganese = 0.01 ppm in the field of dominance of MnOH^+ can be made by assuming that Mn^{+2} is virtually absent. When total manganese activity in solution is 1.0 ppm or more, the MnOH^+ activity is too small to affect the total appreciably.

Comparison of figure 1 with a similar diagram for a system involving water and ferric and ferrous hydroxides (Hem and Cropper, 1959) indicates some interesting points of difference. If the pH of a system is held near 7.0 and the redox potential is increased, the activity of dissolved iron is decreased to less than 0.01 ppm when the Eh exceeds 0.22 v. To decrease the solubility of manganese to the same extent, however, requires an Eh of nearly 0.60 v at a pH of 7.0. Literature on water conditioning and practical experience of water-plant operators in the removal of iron and manganese have shown that removal of manganese by aeration is difficult to accomplish and, in any event, requires a high pH. In some types of water, the results of aeration and removal of iron will include a decrease of pH, which could halt the precipitation of iron and bring the system to equilibrium at a point where troublesome quantities of iron and probably all the original manganese remain in solution.

In water treatment it is essential to maintain conditions that are favorable for rapid-reaction rates. The effect of pH or rates of manganese oxidation will be considered later in this discussion.

LABORATORY STUDIES OF MANGANESE-OXIDATION EQUILIBRIA

The system presented in figure 1 is only approximately applicable to natural water, because other ionic and solid species besides those considered are likely to be present in any natural system. However, the system can be duplicated fairly well in the laboratory and, if the reactions involved are rapid enough, laboratory measurements of Eh, pH, and manganese content should agree with values that would be estimated from figure 1.

A series of six experiments (table 3) was performed to ascertain whether dilute solutions of manganous ions followed the behavior predicted by the theoretical relationships shown in figure 1. A stock solution of manganous ions was prepared by dissolving electrolytically refined metallic manganese in hydrochloric acid and by then driving

off the excess acid by evaporating the solution to dryness. Portions of the resulting manganous chloride stock solution were diluted to a manganous-ion concentration of 10 ppm. The portions were then raised to several selected pH values, ranging from 7.0 to 9.5, by adding sodium hydroxide. The solutions were then allowed to remain in contact with air, and samples were taken from time to time for determination of dissolved manganese by the standard periodate oxidation procedure. Before the manganese concentration was determined, the pH and potential of a bright platinum electrode, assumed to be the Eh of the sample, were measured, and the aliquot was filtered through a plastic-membrane filter whose pore diameter was 0.45μ . Results are given in table 3.

All these solutions tended to reach a constant pH near 7.0 after standing for a day or more. All the manganese was retained in solution except where the initial pH was 9.0 or greater. In most of the solutions the measured potential had a steady upward trend, and after 5 days it was between 0.54 and 0.56 v. The Mn^{+2} in these solutions was oxidized to Mn^{+3} or Mn^{+4} , in part, and these forms precipitated as Mn_2O_3 or MnO_2 , thereby lowering the pH. When the pH became unfavorable for further oxidation, the reactions stopped.

In solution 2, measured and computed potentials remained close together for the entire series of observations (table 3). In solutions 3 to 6, a decided lack of equilibrium was observed at the start of the test. After 30 minutes, equilibrium had returned to solution 3, and after a day to solutions 4 and 5. Solution 4, however, was not in equilibrium at the end of 5 days, but solution 6 was. When measured and computed Eh values agree to ± 0.05 v or less, equilibrium is assumed to have been reached. Previous experience has shown that laboratory measurements of potentials in systems of the kind considered here cannot be reproduced much more closely than this. In most of the solutions at equilibrium, the Eh values agreed within ± 0.05 v.

Figure 1 suggests that at a pH of 7.0 manganese should not precipitate from these solutions unless the Eh exceeds 0.47 but that the solutions brought to a higher pH should lose manganese at lower Eh values. The hydrogen ions produced in the oxidation and precipitation neutralized the solutions and returned them to a pH of 7. Where oxidation had taken place and some manganese precipitated, one would expect a condition of equilibrium to occur after a time, as the system adjusted itself to the new pH and Mn^{+2} levels. This condition is shown by solutions 5 and 6 after 1 day and 5 days, respectively. The solutions that were nearer neutrality originally had measured potentials that are near the level generally expected in aerated water, when measured with the bright platinum electrode. To the extent

that measurements with this electrode system are valid indications of actual redox potentials, the data in table 3 indicate that the equilibrium approach to the study of the chemistry of manganese is a reasonably valid one.

TABLE 3.—*Oxidation of dissolved Mn⁺²*

Solution	Time (hours)	Manganese concentration (ppm)	pH	Eh (volts)	
				Measured	Estimated
1-----	0	10	7.0	0.49	0.48
	.5	10	6.8	.49	.51
	24	9.9	6.8	.58	.51
	120	9.9	7.0	.56	.48
2-----	0	10	7.5	.41	.40
	.5	10	7.3	.45	.43
	24	9.9	6.9	.52	.49
	120	9.8	6.9	.54	.49
3-----	0	10	8.0	.39	.28
	.5	9.8	7.5	.43	.40
	24	9.9	6.7	.51	.53
	120	9.8	6.8	.54	.51
4-----	0	10	8.5	.34	.16
	.5	9.5	7.7	.43	.35
	24	9.9	7.0	.48	.48
	120	9.9	6.9	.54	.49
5-----	0	10	9.0	.26	.05
	.5	8.3	7.8	.43	.33
	24	8.3	7.1	.48	.46
	120	8.0	7.0	.56	.49
6-----	0	10	9.5	.23	.05
	.5	.95	8.3	.42	.29
	24	.85	6.9	.47	.55
	120	.92	7.0	.54	.54

COMPOSITION OF PRECIPITATED OXIDES

The data in table 3 show that very little manganese was precipitated from manganese solutions whose pH remained below 8.5. The behavior of solutions, however, varied with pH. An attempt was made to determine the composition of the oxides precipitated at constant pH.

A series of aliquots containing 10 mg of Mn⁺² each were diluted to about 100 ml, and the pH was increased rapidly to a predetermined value, ranging from 8.5 to 10.0, by adding 0.01 *N* sodium hydroxide. The pH was maintained at the selected value until precipitation appeared to be almost complete; then the precipitates were collected by filtration in sintered glass crucibles and were dried for 1 hour at 180° C. This drying time was sufficient to give a constant weight,

although it could have brought about further oxidation and perhaps dehydration of the precipitate.

The weights of oxide obtained and the apparent percentage of manganese in the precipitates for the indicated pH values were as follows:

pH	Weight of oxide (milli- grams)	Percent Mn
10.0	15.5	64.5
9.5	15.1	66.2
9.0	17.2	58.1
8.5	17.5	57.1

The manganese percentages of the pure oxides and hydroxides for which stability fields are shown in figure 1 are:

Oxide	Percent Mn
Mn(OH) ₂	61.7
Mn ₃ O ₄	72.0
Mn ₂ O ₃	69.6
MnO ₂	63.2

Evidently the precipitates obtained in this experiment do not have the composition of any of the pure oxides. Further investigation was made by preparing a second series of aliquots containing 10 mg of Mn⁺². The oxides were precipitated as before, using pH values of 9.5, 9.0, and 8.5. The precipitates were collected on filter paper and transferred at once to a titration beaker without allowing the precipitate to become dry. Water was added and the suspension was titrated, using a bright platinum electrode and a calomel electrode to indicate the end point potentiometrically. The pH during the titration was maintained near 8.5. A potassium permanganate solution capable of oxidizing 1.66 mg of Mn⁺³ to Mn⁺⁴ per ml was used.

The initial potential in the first of the three titrations, that of the oxide precipitated at a pH of 9.5, was 0.42 v, which is in the Mn₂O₃ stability field. The titration curve had a single inflection point, at about 0.60 v, and the results indicated that about 85 percent of the manganese oxide was in the Mn⁺³ state. The remaining 15 percent probably was in the Mn⁺⁴ state.

In the other two titrations, the initial potential was in the MnO₂ stability field. However, the oxide precipitated at a pH of 9.0 gave a fairly well defined inflection point, again at about 0.60 v, which indicated that about 30 percent of the oxide was of the Mn⁺³ variety. The oxide that precipitated at a pH of 8.5 apparently contained only

Mn^{+4} , because the titration curve displayed no inflection point, even though the potential rose to 0.74 v.

The results of the titrations are interpreted as showing that no Mn^{+2} was present in the oxides either as $\text{Mn}(\text{OH})_2$ or as a part of Mn_3O_4 . If an appreciable amount of Mn^{+2} had been present, the titration curves should have had two inflection points, one representing oxidation of Mn^{+2} to Mn^{+3} and one representing oxidation of Mn^{+3} to Mn^{+4} .

The titration results are not fully conclusive, because some oxidation could have taken place during the process of collecting and filtering the precipitates. The pH value of the water in which two of the precipitates were titrated was from 0.5 to 1.0 unit lower than the pH value at the time the precipitate was formed, and air was not excluded. However, if Mn^{+2} is absent from the titrated oxides, it doubtless is absent also from the dried and weighed oxides.

No combination of MnO_2 and Mn_2O_3 could give a proportion of manganese as low as was obtained for the precipitate formed at pH 8.5 and 9.0. These precipitates must therefore have contained some water. The precipitates formed at pH 9.5 and 10.0 could be mixtures of Mn_2O_3 and MnO_2 or, as seems more likely, could be mostly Mn_2O_3 with some water. The apparent presence of water suggests that the solid present here was partly $\text{Mn}(\text{OH})_3$, which would be 51 percent manganese. If the stability of the hydroxide is similar to that of the oxide, a combination of Mn_2O_3 and $\text{Mn}(\text{OH})_3$ might occur.

The findings on hydration of the oxides represent the composition of material dried at 180°C . Precipitates that are freshly formed, in contact with water, may have different compositions. As noted by Garrels (1960, p. 114) and by others, ferric hydroxide precipitates lose water and decrease in solubility with aging. The behavior of hydrated Mn^{+3} oxides may be similar.

The tendency for manganese to form partly hydrated oxide ores of mixed-valence species is well known and agrees with the behavior noted here. Because the solids formed are not the pure simple oxides that were assumed in preparing figure 1, the laboratory results deviate from those predicted from theory. Of particular interest is the tendency for Mn^{+4} oxide to be precipitated in preference to Mn^{+3} oxide at a pH of 8.5 and an evident tendency for the Mn^{+4} form to be more and more predominant at a lower pH.

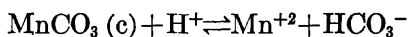
The behavior of manganese in these experiments is in general accord with theoretical calculations used in preparing figure 1. It should be noted that the amount of carbonate-species activity introduced by air is too small to affect the calculations significantly.

MANGANESE EQUILIBRIA INVOLVING BICARBONATE

The anions present in natural water affect the behavior of manganese in various ways. For example, compounds of low solubility may form when manganese combines with carbonate, and complex ions formed by manganese and certain anions may increase the solubility of manganese. Relationships among dissolved and solid species of manganese are likely to be different from those shown in figure 1, if bicarbonate species are present in the system, and such species are present in practically all natural water because of the widespread availability of carbon dioxide.

FIXED BICARBONATE ACTIVITY

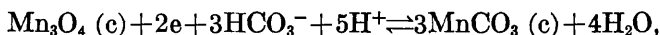
Figure 2 was prepared from base data in tables 1 and 2. The presence of a constant total activity of bicarbonate species equivalent to 100 ppm in HCO_3^- was assumed. This represents a system that is sealed from contact with air or from other sources that could supplement the amount of carbon dioxide initially present. Many of the relationships in figure 2 are the same as in figure 1. However, the equilibrium



affects a considerable part of the area of figure 2. The equilibrium constant for this equation depends on the form to which the solid is assigned. If the form is rhodochrosite, the constant is 0.31 [ΔF° for rhodochrosite from Mah (1960)]. If it is precipitated MnCO_3 , the constant is 1.0, by using the ΔF° value of Garrels, Thompson, and Siever (1960). For figure 2, the form was assumed to be rhodochrosite. The pH at which Mn^{+2} activity is 1.8×10^{-7} molal is then computed to be 9.0.

Garrels, Thompson, and Siever attribute the difference between ΔF° values for rhodochrosite and for precipitated MnCO_3 to impurities in the natural rhodochrosite.

Free-energy data show that the boundary between rhodochrosite and $\text{Mn}(\text{OH})_2(c)$ is at a pH of 11.7. Thus, the carbonate field occupies virtually all the MnOH^+ field of figure 1 and infringes on the $\text{Mn}(\text{OH})_2(c)$ area. The boundary between $\text{Mn}_3\text{O}_4(c)$ and $\text{MnCO}_3(c)$ shown in figure 2 was computed from the relationship



where $E^\circ = 1.87$.

The activity of the specific bicarbonate species present in the system is a function of pH and can be calculated from the two dissociation constants for H_2CO_3 given in table 2 and the amount specified to be

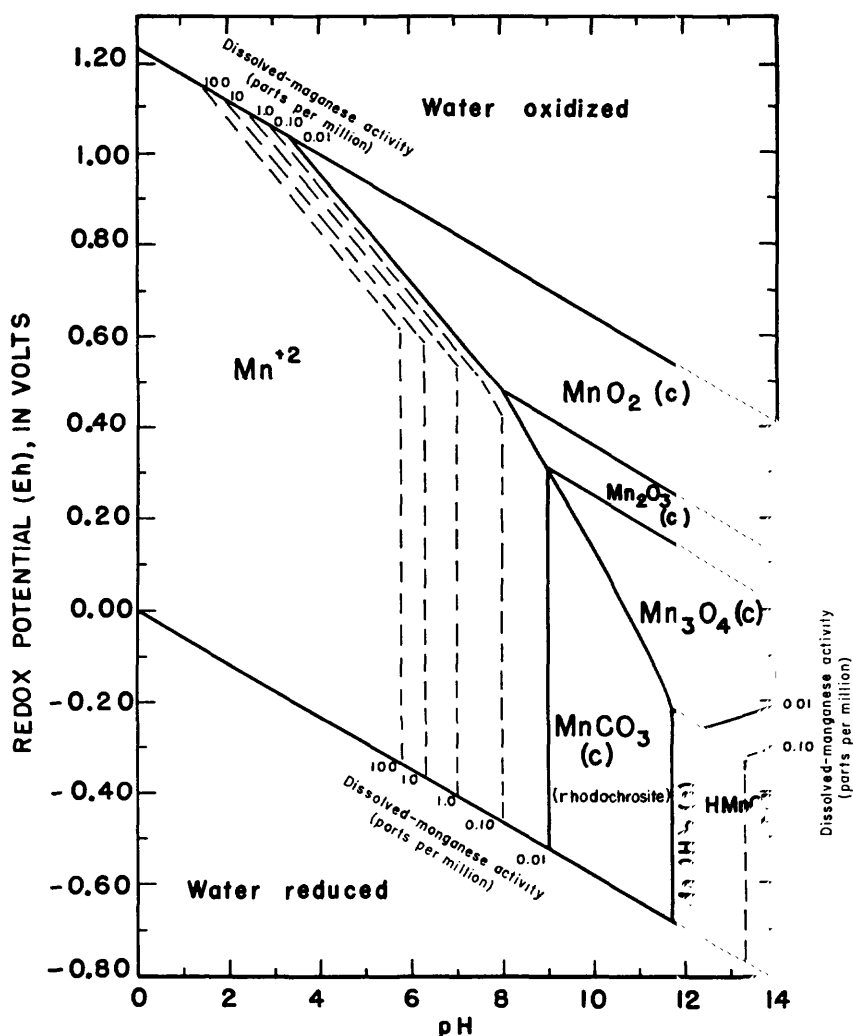
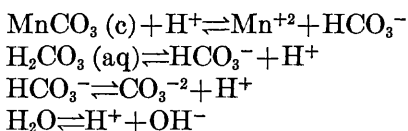


FIGURE 2.—Stability fields of manganese species in aqueous solution free of sulfate. Total dissolved-manganese activity ranges from 0.01 to 100 ppm. Bicarbonate-species activity is 100 ppm as HCO_3^- . Symbol (c) indicates crystalline form.

present (100 ppm as HCO_3^-). As the activity of bicarbonate decreases with increasing pH above 8.2, the MnCO_3 (c)— Mn_3O_4 (c) boundary curves somewhat.

The activity of bicarbonate ions must be known to compute the positions of the dashed vertical lines in figure 2 that represent the MnCO_3 (c)— Mn^{+2} boundary at Mn^{+2} activities of 0.10, 1.0, 10, and 100 ppm. An exact treatment would involve considering simultaneously the equilibria



and possibly others. The dissociation constants for carboric acid however, show that when pH ranges from 7 to 9 the bicarbonate ion predominates over the carbonate ion or the undissociated carbonic acid by a factor of at least 10 to 1. In this pH range, the dissociation of water is also a minor factor. Consequently, the boundaries that define manganese activities of 0.01, 0.10, and 1.0 ppm can be located with satisfactory accuracy by assuming that all the bicarbonate activity is present as HCO_3^- . These boundaries are at pH 9.0, 8.0 and 7.0.

Boundaries for activities of 10 and 100 ppm of dissolved Mn^{+2} must be located by considering both HCO_3^- and H_2CO_3 species. At a pH of 6.4, as indicated by the dissociation constant in table 2, half the total bicarbonate species will be present as HCO_3^- and half as undissociated $\text{H}_2\text{CO}_3(\text{aq})$. At a pH of 5.4, the HCO_3^- form is only about 10 percent of the total. As a result of decreased availability of bicarbonate ions, the solubility of $\text{MnCO}_3(\text{c})$ increases at an increasing rate as the pH becomes less than 6.4 and the spacing between the manganese-solubility lines decreases.

If the precipitated form of manganese carbonate rather than the natural rhodochrosite is present, the stability field of the solid is decreased in size considerably. The boundary between dissolved Mn^{+2} and the solid at 0.01 ppm activity of manganese would be shifted to the right a half pH unit to 9.5, and the boundary between the solid manganese carbonate and the solid $\text{Mn}(\text{OH})_2$ would be at a pH of 11.4. The positions of the boundaries for such a system are shown in figure 3. Computations are the same as for those for figure 2, except that when $\text{MnCO}_3(\text{c})$ is involved the free-energy value used is the same as that for precipitated material, -194.7 kilogram-calorie per mole.

Natural water frequently contains activities of 100 ppm or more of bicarbonate. Many carbonate rocks contain some manganese. The equilibria involving carbonate are likely, therefore, to have much practical importance. The behavior of manganese in natural water is indicated approximately by figures 2 and 3, although in nature the systems are more complex than the simple ones represented here. However, the effects of carbonates may help to explain why natural water seldom contains more than 1 ppm of manganese. Figure 1 indicates manganese solubility to be considerably greater than 1.0 ppm in most of the Eh-pH area common to natural water—for

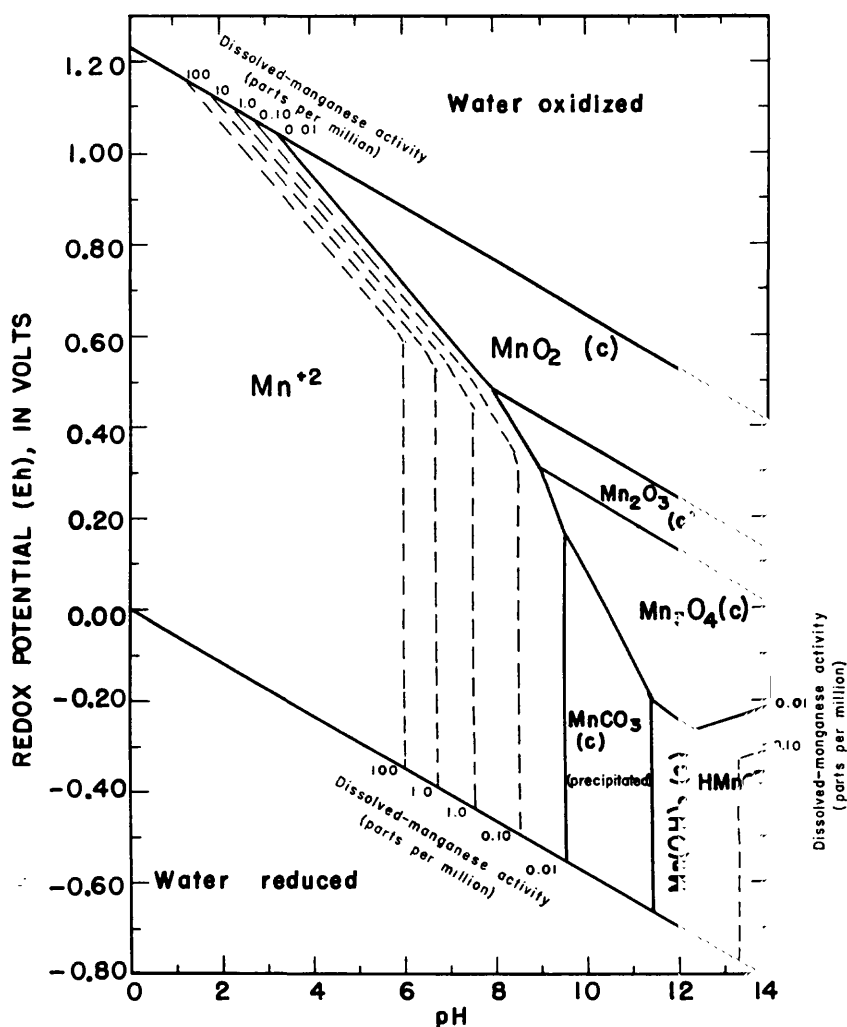


FIGURE 3.—Stability fields of manganese species in aqueous solution. Conditions are the same as in figure 2 except that precipitated MnCO_3 is substituted for rhodochrosite. Symbol (c) indicates crystalline form.

example, from pH 6.0 to 8.5 and from Eh +0.45 to -0.20. In a similar area in figures 2 and 3, the solubility exceeds 1.0 ppm only below pH 7 or pH 7.5, respectively. A higher bicarbonate activity than 100 ppm would, of course, decrease the solubility of manganese still further.

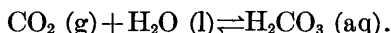
In the systems represented in figures 2 and 3, the supply of bicarbonate or related species is fixed at a single and constant value. Such a fixed value might be attained in an aquifer that does not contain a gas phase or any carbonate minerals. However, any change of pH in a natural system containing carbonate rocks will alter the

amount of dissolved bicarbonate, so that the model is not entirely congruent with all natural conditions.

FIXED CARBON DIOXIDE PARTIAL PRESSURE

Another type of system involving the same solids and ions as those in figure 3 is one in which a gas phase is in contact with an aqueous phase and the partial pressure of carbon dioxide is at a fixed value. In this system, the amounts of bicarbonate species available in solution are a function of the pH and the partial pressure of CO_2 and are related to the form of solid manganese carbonate and the amount of dissolved manganese present. Figure 4 represents a system exposed to laboratory air. The solid MnCO_3 is the freshly precipitated variety. The literature indicates that pure air contains 0.03 percent CO_2 by volume. The carbon dioxide content of air obtained from the laboratory compressed-air line was found to be 0.047 percent by volume. The atmospheric pressure is affected by the fact that the laboratory is west of Denver, Colo., at an altitude of about 5,600 feet above sea level. Therefore, when the barometric pressure is in the general fair-weather range, the partial pressure of carbon dioxide in the laboratory air is approximately 3.8×10^{-4} atmosphere.

Accordingly, the value for $p\text{CO}_2$ (partial pressure of CO_2) used in preparing figure 4 was 3.8×10^{-4} . To apply this value in the calculations, the fundamental equation is



A value for the equilibrium constant can be obtained by using free-energy data in table 1 and the relationship

$$-RT \ln K = \Delta F^0.$$

For this equilibrium, the value of K is 3.7×10^{-2} . Hence,

$$[\text{H}_2\text{CO}_3] = 3.7 \times 10^{-2} \times p\text{CO}_2,$$

and the activity of $\text{H}_2\text{CO}_3 (\text{aq})$ available in the solution would be 1.4×10^{-5} molal.

The chemical equilibria for the first and second dissociation of H_2CO_3 must be satisfied in this system. Hence,

$$\frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]} = 4.16 \times 10^{-7},$$

$$\frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} = 4.84 \times 10^{-11}.$$

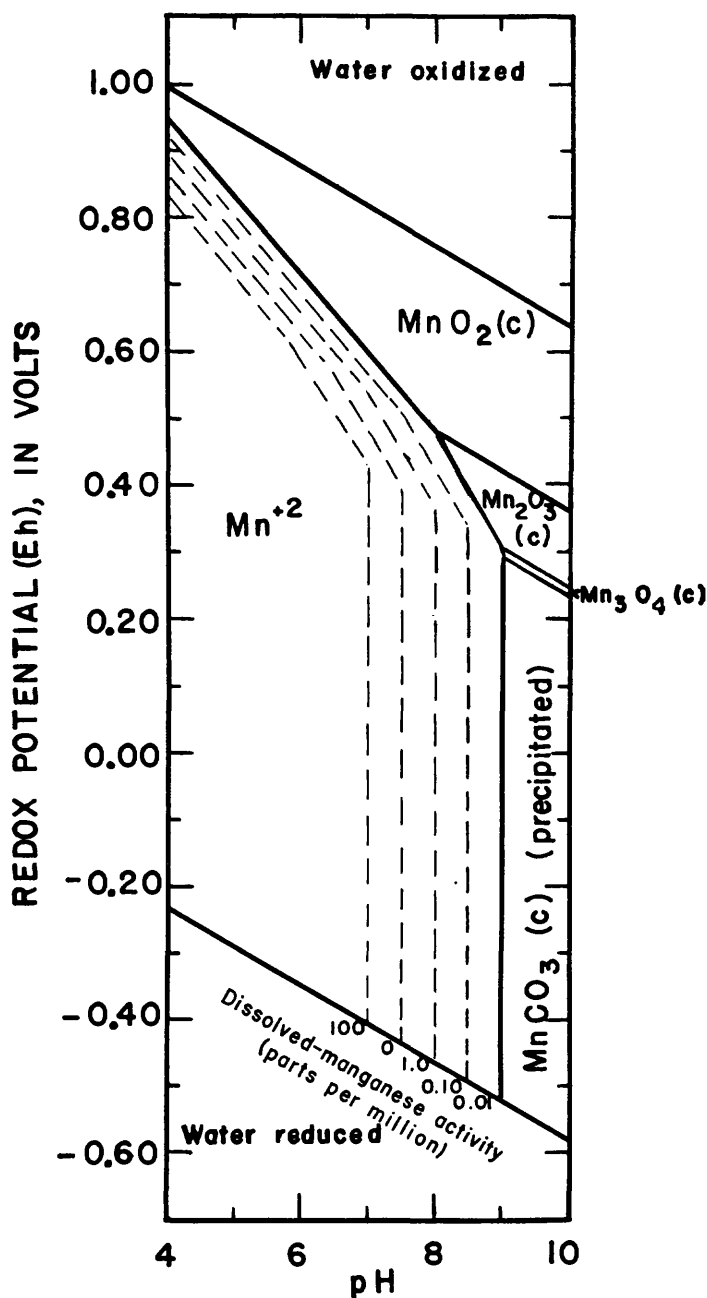


FIGURE 4.—Stability fields of manganese species in aqueous solution in the pH range from 4.0 to 10.0. The solution contains no sulfate. Dissolved-manganese activity ranges from 0.01 to 100 ppm at a constant partial pressure of $CO_2 = 3.8 \times 10^{-4}$ atmosphere. Symbol (c) indicates crystalline form.

Also, the equilibrium equation for solution of precipitated MnCO_3 applies

$$\frac{[\text{Mn}^{+2}][\text{HCO}_3^-]}{[\text{H}^+]} = 1.0,$$

and the ionic product of water is involved

$$[\text{H}^+][\text{OH}^-] = 10^{-14}.$$

For electrical neutrality, the actual concentrations of negative and positive ions present must be equivalent, and we may write

$$2C_{\text{Mn}^{+2}} + C_{\text{H}^+} = 2C_{\text{CO}_3^{-2}} + C_{\text{HCO}_3^-} + C_{\text{OH}^-},$$

where C represents molar concentration.

For all practical purposes, the activity coefficients may be assumed to be unity in the dilute solution under consideration, and activities may be substituted for concentrations in the preceding equation.

The treatment can be simplified considerably in locating the MnCO_3 (c)- Mn^{+2} boundary, where $[\text{Mn}^{+2}] = 1.8 \times 10^{-7}$. This is in the pH range where the concentrations of CO_3^{-2} and OH^- can be neglected. Hence,

$$[\text{HCO}_3^-] = \frac{4.16 \times 10^{-7} \times [\text{H}_2\text{CO}_3]}{[\text{H}^+]} = \frac{6.0 \times 10^{-12}}{[\text{H}^+]},$$

$$[\text{HCO}_3^-] = \frac{[\text{H}^+]}{[\text{Mn}^{+2}]} = \frac{[\text{H}^+]}{1.8 \times 10^{-7}}.$$

Hence

$$\frac{[\text{H}^+]}{1.8 \times 10^{-7}} = \frac{6.0 \times 10^{-12}}{[\text{H}^+]}$$

$$[\text{H}^{+2}] = 1.08 \times 10^{-18}$$

$$[\text{H}^+] = 1.04 \times 10^{-9}$$

$$\text{pH} = 9.0.$$

As the pH of this system decreases, the solubility of MnCO_3 (c) increases rapidly. However, as the pH increases, the dissolved carbonate in the system also increases, and, as a result, the stability field for MnCO_3 (c) occupies a large area, which includes the fields of $\text{Mn}(\text{OH})_2$ (c), HMnO_2^- , and most of Mn_3O_4 (c). The significance of the effects at a high pH is not great in natural water because water open to the atmosphere rarely would have a pH greater than 9.0. The pH range shown in figure 4 is from 4.0 to 10.0.

LABORATORY STUDIES

A series of 10 experimental solutions was prepared to check the position of the boundaries in figures 2 and 3. The solutions each

contained 10 ppm Mn^{+2} and 100 ppm HCO_3^- . The pF of each solution was adjusted with a potassium hydroxide solution to a predetermined value ranging from 6.5 to 11.0, and the solutions were transferred to glass-stoppered bottles. The bottles were filled completely so that no air space remained. The solutions were allowed to stand undisturbed for 13 days, after which the pH and the Eh were measured. To remove precipitated material from them, the solutions then were filtered through plastic-membrane filters with a pore-diameter of 0.45 μ .

Only the solutions at a pH of 8.0 or less had Eh and pH values in the stability region for MnCO_3 (c) (precipitated) in figure 3. Some light-colored precipitate identified as manganese carbonate was filtered out of the solutions held at pH 7.5 and pH 8.0. In the solutions held at higher pH, a brown or black precipitate of oxide was obtained. This is to be expected, because the pH and Eh of these solutions plot in the oxide-stability region.

Although figure 3 indicates that manganese carbonate solubility is less than 10 ppm in terms of activity at pH 7.0, no precipitate appeared in the solution at that pH. The activity of Mn^{+2} in the solution was also less than 10 ppm, owing to the amounts of other ions present; hence, this solution approached equilibrium closely and precipitation should not have been expected.

In an attempt to obtain carbonate precipitates at higher pH, another set of solutions containing manganese and bicarbonate was prepared. To maintain a low redox potential, 4,000 ppm of hydroxylamine hydrochloride was added to each solution. Manganese carbonate was precipitated from the solutions having a pH greater than 8.0. However, the large amount of hydroxylamine in these solutions probably influenced the behavior of the manganese in other ways besides altering the Eh. Consequently, the results cannot be used to verify the positions of solubility lines on figure 3.

MANGANESE EQUILIBRIA INVOLVING SULFATE

Manganous sulfate is a readily soluble compound. However, if a solution containing manganese and sulfate ions were subjected to a strongly reducing environment, in which sulfate ions would be reduced to sulfide, a precipitate of relatively insoluble manganese sulfide could be formed. The behavior of manganese in such systems is affected, therefore, by redox reactions involving sulfur.

Equilibria involving sulfur species have been discussed by Garrels and Naeser (1958). Sulfur can exist at oxidation states ranging from -2 to $+6$; and, because of the covalent character of sulfur bonding, some species apparently have fractional oxidation numbers. Thermo-

dynamic calculations, however, show that at equilibrium in water at 25°C and 1 atmosphere pressure the stable species are S^{-2} , S^{-1} , S^0 , and S^{+6} and that the situation is not complicated by the intermediate oxidation states, such as thiosulfate or sulfite.

Occasionally, some of the partially oxidized species of sulfur are reported in published water analyses. Generally the analyses represent thermal springs to which the calculations for 25°C and 1 atmosphere pressure do not apply. Metastability, however, is characteristic of sulfur species in nonthermal environments. Hence, the assumption that equilibrium generally exists for sulfur species in natural water is less justified than for many other dissolved constituents. Some reactions involving sulfur are very slow when catalysts are absent. The reduction of sulfate, for example, although of fairly common occurrence in ground water, does not seem to take place unless anaerobic bacteria of a suitable type and a supply of organic food for the bacteria are present.

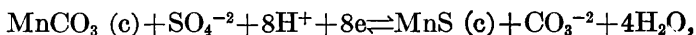
The stability-field diagram is, nevertheless, a valuable indicator of limiting conditions for systems that contain sulfur. Figure 5 represents a system containing activities of 10 ppm dissolved- CO_2 species as bicarbonate and 1,000 ppm dissolved-sulfur species as sulfate. Solids represented besides the oxides and hydroxide of manganese in figure 1 include the rhodochrosite form of manganese carbonate and crystalline manganese sulfide (MnS). The free energy of formation of the polysulfide MnS_2 corresponding to pyrite is not known; hence, this variety was not considered.

Figure 5 shows that an area of stability exists for MnS (c) at a high pH and under strongly reducing conditions. However, it is essential that the activity of sulfur species be very much greater than the activity of bicarbonate species. When the activities of both sulfur and bicarbonate species are equal to 100 ppm, the MnS (c) field disappears.

Boundaries for the carbonate, oxide, and hydroxide species in figure 5 were calculated from equations used for previous illustrations. The positions of the boundaries are somewhat altered from those of figures 2 and 3 because of the low bicarbonate activity. Boundaries between the MnS (c) field and the fields of the other solids were determined from two equilibria



where $E^0 = 0.36$ v, and



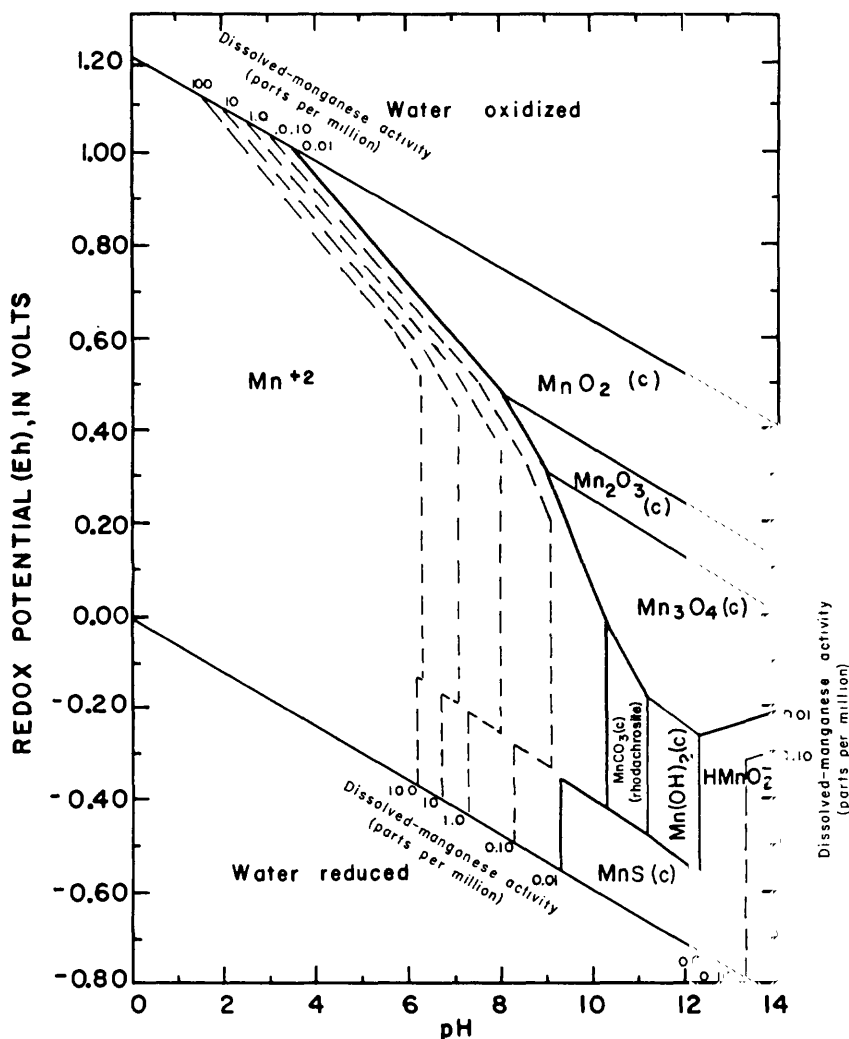
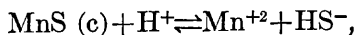


FIGURE 5.—Stability fields of manganese species in aqueous solution. Total dissolved manganese activity ranges from 0.01 to 100 ppm; bicarbonate species activity is 10 ppm as HCO_3^- ; and sulfur species activity is 1,000 ppm as SO_4^{2-} . Symbol (c) indicates crystalline form.

where $E^0 = 0.17$ v. As the pH decreases, MnS is dissolved to yield Mn^{+2} , as in the equilibrium



where $K = 4.13$, or in the equilibrium



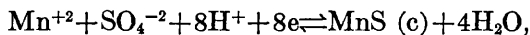
where $K = 4.14 \times 10^7$.

At high pH, the sulfide may go into solution to yield manganite ions, as in the equilibrium

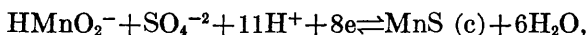


where $K = 1.8 \times 10^{-34}$.

Sloping boundaries between MnS (c) and the fields of dominance of Mn^{+2} and HMnO_2^- are defined by the equilibria

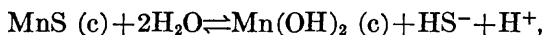


where $E^0 = 0.25$ v, and



where $E^0 = 0.50$ v.

At a high pH, the MnS (c) boundary is affected by the relation



where $K = 2.0 \times 10^{-15}$.

Hence, when the pH value is greater than about 13.0 and when the activity of the sulfur species is 1,000 ppm, the MnS (c) field is replaced by the Mn(OH)_2 (c) field.

LABORATORY STUDIES

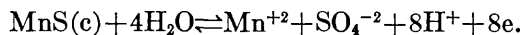
An experiment was performed in the laboratory to evaluate the behavior of manganese sulfide. A few hundred milligrams of managanous sulfide was prepared by bubbling H_2S gas through manganese chloride solution. The prepared material was put into a bottle, and 1 liter of de-ionized distilled water was added. The mixture was continuously agitated by air bubbled into the bottle from the laboratory compressed-air line. From time to time, samples of the solution were withdrawn, and their pH, Eh, and manganese content were determined. Results are given as follows:

<i>Time (hours)</i>	<i>Dissolved manganese (ppm)</i>	<i>pH</i>	<i>Eh (volts)</i>
3-----	4.2	-----	-----
24-----	8.2	7.4	0.16
48-----	10	7.4	.23
72-----	10	7.2	.08
144-----	11	7.2	.09
312-----	14	7.2	.36
480-----	13	7.0	.39

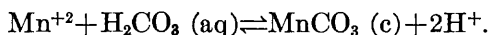
Although the Eh throughout the experiment was favorable for sulfide oxidation, the amount of manganese dissolved did not increase

continuously but seemed to reach a fairly stable value. The fluctuations of Eh suggest that if an equilibrium was reached, it was one that did not necessarily involve redox potential.

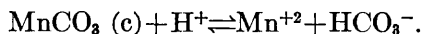
The simplest explanation of the results seems to be that a two-step reaction occurred in which the manganous sulfide was converted to carbonate that then partly dissolved. The first reaction that took place was oxidation of the manganous sulfide



However, the air bubbled through the solution contained some carbon dioxide that, as it dissolved, tended to precipitate manganese as the carbonate



Thus, manganous sulfide dissolved and manganous carbonate precipitated. The first reaction practically ceased after a protective coating of carbonate formed on the sulfide particles. The ultimate equilibrium involving only pH, dissolved manganese, and bicarbonate activity would be



If the partial pressure of CO_2 in the air remained constant, a constant $[\text{H}^+]$ would be attained. The ionic strength of the final solution is not known and temperature was not considered. However, the temperature did not vary greatly and was very near 25°C throughout the experiment. If it is assumed that the concentrations are low enough so that the activity coefficients of the dissolved ions are equal to unity, the observed pH- and dissolved- Mn^{+2} values should agree closely with the manganese-solubility lines in figure 4, which represents a system containing $\text{MnCO}_3 (\text{c})$ (precipitated) exposed to air.

Figure 4 suggests that a solubility of 10 ppm Mn^{+2} ought to occur at a pH of 7.5. The 24- and 48-hour values represent a very close approach to these conditions and are evidence that an equilibrium may be reached. Later observations in the experiment seem to indicate conditions further from equilibrium, but the relatively small deviations may result from changes in composition of the air or contamination during the rather long period that air was continuously bubbled through the solution.

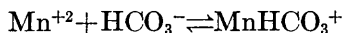
SOLUBLE MANGANESE COMPLEXES

The solubility of manganese can be considerably affected by formation of complexes or ion-pairs in solutions where certain anions com-

mon in natural water are present. The effects of these require consideration in studies of chemistry of manganese.

MANGANESE BICARBONATE COMPLEX

Bjerrum, Schwarzenbach and Sillén (1958) refer to a 1942 publication by Näsänen reporting the existence of a complex cation with the formula MnHCO_3^+ . The equilibrium constant for the reaction by which this complex ion is formed



is given as 3.0×10^3 . The equilibrium constant was obtained by experiments conducted in a rather strong sodium chloride solution.

The published value for the equilibrium constant implies a strong complexing action. Direct application of this value to relatively dilute solutions, such as those considered in figure 2, suggests that the complex often is the dominant manganese species present. For example, in a solution with a bicarbonate activity of 3.3×10^{-3} molal, the ratio $[\text{MnHCO}_3^+]:[\text{Mn}^{+2}]$ will be about 10, as long as the total manganese activity remains small compared to the bicarbonate activity. An activity of 3.3×10^{-3} molal of the bicarbonate amounts to a little more than 200 ppm and is a value commonly attained in natural water.

LABORATORY STUDIES

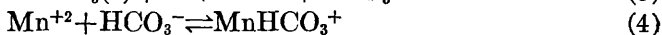
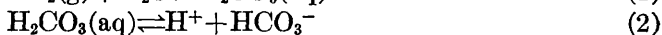
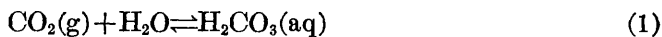
Because of the possible importance of the bicarbonate complex in the chemistry of manganese in natural water, some laboratory work was done to check the equilibrium constant. The value reported in the literature (3.0×10^3) was obtained under conditions different from those of the investigations for this report.

In the first experiment, about 10 g of analytical-grade manganese carbonate powder was placed in a glass reaction jar containing 1,000 ml of de-ionized distilled water. The jar was fitted with a large rubber stopper. Through holes in the stopper a glass electrode, a calomel electrode, and a thermometer were introduced into the solution. Carbon dioxide gas was bubbled into the solution through a glass tube reaching to near the bottom of the jar. A fifth hole in the stopper served as a vent for excess carbon dioxide. The electrodes were connected to a pH-meter, and the gas flow was started. The pH slowly decreased as the carbon dioxide in solution in the water caused some of the manganese carbonate to dissolve. After about 4 hours, the pH reached a value of 5.37 and remained at that value during an additional 12 hours that CO_2 was bubbled through the solution. The apparent chemical equilibrium of the reaction was tested by making periodic determinations of the manganese content of the solution after

filtration through a plastic-membrane filter whose pore diameter was 0.45μ . The manganese content appeared to remain constant near 80 ppm for the last 8 hours of the experiment.

The reaction vessel was exposed to minor temperature fluctuations in the laboratory, but the equilibrium pH was reached at a temperature between 24° and 25° C. Hence, no temperature correction to standard conditions (25° C) was made. The pressure on the system was about 0.85 atmosphere, because the altitude of the laboratory is 5,600 feet. This departure from standard conditions affects the carbon dioxide equilibrium but is not otherwise significant.

In the experiment, the following chemical relationships were at equilibrium:



The value of K for equilibrium (1), calculated previously for the experiment in which air was bubbled into a solution containing MnS (c) is 3.7×10^{-2} . The molal activity of H_2CO_3 , calculated for the pressure at the altitude of the laboratory, is 3.1×10^{-2} .

The activity of bicarbonate can then be calculated for the equilibrium pH of 5.37 from equilibrium (2), using the equilibrium constant in table 2

$$[\text{HCO}_3^-] = \frac{4.16 \times 10^{-7} \times 3.1 \times 10^{-2}}{4.3 \times 10^{-6}} \\ = 3.0 \times 10^{-3} \text{ molal.}$$

This value can be used with equilibria (3) and (4) to compute the activity for Mn^{+2} and MnHCO_3^+ . The equilibrium constant for equilibrium (3), however, must be computed first, and to do so one must select a value of the standard free energy of formation of precipitated MnCO_3 (c).

A series of experiments that are virtually the same as the one done here has been reported by Garrels, Thompson, and Siever (1960). The equilibrium pH for their precipitated MnCO_3 was 5.35. The value of 5.37 obtained here is considered a reasonable check, and the value reported by Garrels, Thompson, and Siever for the free energy of formation of MnCO_3 is evidently nearly applicable to the material used here. The equilibrium constant determined from equilibrium (3) is 1.0, and the free-energy value is given in table 1.

To complete the solution of equilibria (3) and (4), activities for the dissolved manganese species Mn^{+2} and MnHCO_3^+ are needed. The

analytical value for manganese is a concentration rather than an activity and also is a total of all dissolved manganese species. Activity coefficients for the two ions can be computed from concentrations with the Debye-Hückel limiting law, using the method of Klotz (1950). The basic equation is

$$\log \gamma = \frac{-Az^2\sqrt{\mu}}{1 + Ba\sqrt{\mu}}$$

where

γ = activity coefficient sought

z = ionic charge

μ = ionic strength of solution

A = a constant relating to solvent (0.5085 for water at 25 °C)

B = a constant relating to solvent (0.3281×10^8 for water at 25 °C)

a = effective diameter of ion of charge z .

Ionic strength is computed from the equation

$$\mu = \sum \frac{m_i z_i^2}{2},$$

where m_i represents the concentration of each different ion, in moles per liter and z_i is the charge of that ion.

In the experimental solution, the total concentrations of the ionic species that contribute to ionic strength are divided among univalent and divalent forms. If no complexing occurred, all the 80-ppm-determined manganese could be assigned to Mn^{+2} . The ionic strength computed from this and from the bicarbonate activity, which probably does not differ greatly from the concentration, would be

$$\begin{aligned} \mu &= \frac{3.0 \times 10^{-3}}{2} + \frac{1.5 \times 10^{-3} \times 4}{2} \\ &= 4.5 \times 10^{-3}. \end{aligned}$$

If all the manganese were complexed, the ionic strength would be 2.25×10^{-3} .

Thus the upper and lower limits of the value for μ can be determined. However, the exact value that should be used cannot be determined until the proportion of the complexed to uncomplexed species of dissolved manganese is known.

The experimental data provide a means for checking the validity of the published value of K , 3.0×10^3 for equilibrium (4). The

activity of bicarbonate is already available, from equilibria (1) and (2), and is 3.0×10^{-3} . Therefore,

$$\frac{[\text{MnHCO}_3^+]}{[\text{Mn}^{+2}]} = 3.0 \times 10^{-3} \times 3.0 \times 10^3 = 9.$$

This ratio of activities is somewhat larger than the ratio of actual concentrations because the activity coefficients for the two species are not the same. However, for present purposes, the difference is not important. Complexing would be extensive and the ionic strength of the solution is therefore about 2.5×10^{-3} . Substitution of this value for μ in the Debye-Hückel equation gives activity coefficients of 0.82 for Mn^{+2} and 0.95 for HCO_3^- and MnHCO_3^+ . The value of α in the Debye-Hückel equation for the complex ion is assumed to be the same as that given for HCO_3^- by Klotz (1950).

The total molal concentration of manganese present, 1.5×10^{-3} includes the two ionic species. Therefore,

$$C_{\text{Mn}} = C_{\text{Mn}^{+2}} + C_{\text{MnHCO}_3^+} = 1.5 \times 10^{-3}, \quad (5)$$

where C represents measured molal concentrations. The concentrations of the two species are converted to activities by means of the activity coefficients:

$$1.5 \times 10^{-3} = \frac{[\text{Mn}^{+2}]}{0.82} + \frac{[\text{MnHCO}_3^+]}{0.95}$$

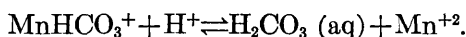
From this relationship and from the ratio of the activities of complexed to uncomplexed manganese in equilibrium (4) the two activities can be evaluated. Simultaneous solution of the two equilibria gives 1.4×10^{-4} for $[\text{Mn}^{+2}]$. Substitution of this value in equilibrium (3), together with the previously computed bicarbonate activity and the equilibrium pH of 5.37 gives an equilibrium constant of 9.9×10^{-2} , compared with the value of 1.0 computed from free-energy data.

Obviously, complexing in the system falls far short of the degree predicted by the reported constant for equilibrium (4). If, as a limiting factor, no complexing is assumed and the measured manganese concentration corrected to activity is used in equilibrium (3), the value for K obtained is 0.84—a near approach to 1.0, the computed value. However, to assign any manganese to the complex form would lower the value for the computed K even further. Evidently, the amount of complex present is small, but a more refined experimental procedure is needed to evaluate the system.

At least three possible explanations could be offered for the apparent lack of complexing: (1) the complexing reaction is slow and had not

reached equilibrium when the pH reached a constant value (this explanation is rather unlikely); (2) the complex form is less stable than the published data indicate; and (3) in filtering the solution before determining Mn^{+2} , some dissolved manganese was precipitated. Any or all these factors might influence the results.

Several approaches can be used to learn more about the importance of the complex. If the solutions containing bicarbonate and the manganese bicarbonate complex are titrated with standard acid, as in the alkalinity titration made in a routine water analysis, the breakdown of the complex can be represented as



The equilibrium constant for this reaction is 7.2×10^2 if the standard free energy of formation of the complex is taken as -199.5 kg-cal, the value that is obtained from the published data on the complex. From this equation it can be shown that the pH at which the activities of the complexed and uncomplexed varieties are equal is about 4.3, where the total of bicarbonate and dissolved CO_2 species present is 3.4×10^{-2} molal. The equilibrium solution under study should have about this activity of bicarbonate and related species, mainly in the form H_2CO_3 (aq). The end point of the titration would be well below a pH of 4.

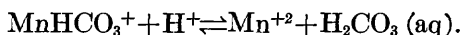
Thus, a solution containing the complex would have a buffering capacity below a pH of 4.5, the usual end point of the alkalinity titration if the free energy of the complex were as low as indicated by the published data. The behavior of solutions during alkalinity titration should give evidence regarding the complex, but the system in equilibrium at 1 atmosphere of pressure of CO_2 is not easy to evaluate in this way.

Accordingly, another set of solutions was made up to permit a longer time for complexing to take place, to provide more favorable systems for titration, and to avoid filtration of the sample used for manganese determination.

DETERMINATION OF EQUILIBRIUM CONSTANT

A system containing water, solid manganese carbonate, and carbon dioxide gas at 1 atmosphere pressure was allowed to come to equilibrium (constant pH). Aliquots containing solution and solid were poured off into glass-stoppered bottles. The bottles were filled completely so that no gas space remained, and the aliquots were allowed to stand until the solution cleared. Portions were then taken from the bottles at predetermined times, and manganese and alkalinity were determined.

The equilibria involved in these solutions were Nos (2), (3), and (4), and probably



Because no gas phase is present, however, equilibrium (1) is not applicable. The only constituent available in excess is now the solid MnCO_3 (c) and the system ought to reach a pH that is controlled by equilibrium (3), with the balance between HCO_3^- and H_2CO_3 (aq) adjusting itself accordingly. The amounts of manganese complexed can be determined from analyses of the solution and from equilibrium computations.

After 3 days, the pH of the clear solution was determined to be 5.48, and an aliquot was titrated with standardized sulfuric acid. The bicarbonate content so determined was 235 ppm. Manganese content was determined to be 93 ppm. The value for bicarbonate includes both HCO_3^- and MnHCO_3^+ , and the value for manganese includes both Mn^{+2} and MnHCO_3^+ . From the Debye-Hückel limiting law the activities of the four principal ionic species present can be estimated. For this calculation, the Mn^{+2} and HCO_3^- ions were assumed to dominate the system. Thus the total ionic strength can be estimated closely from the concentrations for total manganese and bicarbonate species. The value obtained for ionic strength is 0.0054. The activity coefficient (γ) for Mn^{+2} is computed to be 0.76 and for the bicarbonate and also the complex is computed to be 0.93.

The amount of manganese complexed can be evaluated by a method of successive approximation. Assume first that no complexing has occurred. Activity data then can be substituted in equilibrium (3), as follows:

$$\frac{[\text{HCO}_3^-][\text{Mn}^{+2}]}{[\text{H}^+]} = K$$

$$[\text{H}^+] = 3.31 \times 10^{-6}$$

$$[\text{HCO}_3^-] = 3.85 \times 0.93 \times 10^{-3} = 3.58 \times 10^{-3}$$

$$[\text{Mn}^{+2}] = 1.69 \times 10^{-3} \times 0.76 = 1.28 \times 10^{-3};$$

hence,

$$K = \frac{3.58 \times 10^{-3} \times 1.28 \times 10^{-3}}{3.31 \times 10^{-6}} = 1.38$$

The equilibrium constant, K , however, should be 1.0, as computed from free-energy data. The difference is assignable to complexing that has affected the activities of Mn^{+2} and HCO_3^- .

The activity value for manganese (uncomplexed) then is lowered by a suitable amount, and the concentration represented by this activity, calculated from the relation

$$C_{\text{Mn}^{+2}} = \frac{[\text{Mn}^{+2}]}{\gamma}$$

An equivalent concentration of bicarbonate is assigned to this concentration of manganese, and its activity is computed. The activity is subtracted from $[\text{HCO}_3^-]$ in equilibrium (3), and a new value for K is calculated. The procedure is repeated, if necessary, until the value of K obtained is 1.0. The amount of complexed manganese in terms of concentration is thus calculated to be 3.3×10^{-4} molar or 18 ppm. The ratio of activities of complexed to uncomplexed manganese in this solution is 0.24. From equilibrium (4), the equilibrium constant K_{complex} for the formation of the complex is computed to be 75.

The analysis and computation was repeated three times, after the solutions had stood for longer periods. The results are given in table 4.

TABLE 4.—*Experimental data on manganese bicarbonate complex*

Test	Reaction time (hours)	Concentration (ppm)		Activities (moles per liter)			Calculated K (equilibrium 3)	Concentration of complexed manganese (moles per liter)	$\frac{[\text{MnHCO}_3^+]}{[\text{Mn}^{+2}]}$	K_{complex}^1
		C_{Mn}	C_{HCO_3}	$[\text{Mn}^{+2}]$	$[\text{HCO}_3^-]$	$[\text{H}^+]$				
1-----	49	93	234	1.28×10^{-3}	3.58×10^{-3}	3.31×10^{-6}	1.37	3.3×10^{-4}	0.24	75
2-----	150	78	190	1.11×10^{-3}	2.90×10^{-3}	2.75×10^{-6}	1.17	1.4×10^{-4}	.11	40
1a-----	216	83	220	1.16×10^{-3}	3.36×10^{-3}	3.16×10^{-6}	1.23	2.1×10^{-4}	.15	51
2a-----	360	64	141	0.91×10^{-3}	2.17×10^{-3}	1.58×10^{-6}	1.25	1.7×10^{-4}	.17	85

¹ Mean value for $K_{\text{complex}} = 63$.

Tests 1 and 1a represented solutions with an excess of solid MnCO_3 present and no gas phase. Tests 2 and 2a were made on the same two sample bottles, but because some solution was taken out in the earlier runs, a gas phase was present. The bottles were kept stoppered while standing. The loss of bicarbonate and increase in pH was related in part to equilibration of the dissolved CO_2 with a portion of previously dissolved CO_2 that had migrated to the gas phase. At the same time, the amount of manganese present readjusted itself to the new pH and bicarbonate levels, with precipitation of manganese carbonate. Because the calculated data agree fairly well for all four tests, it seems likely that equilibrium was reached.

When the usual end point of a pH of 4.5 was approached during the titration of alkalinity in the samples, their behavior was unlike

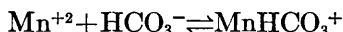
that usually observed. The pH decreased as the titration proceeded and exhibited the usual inflection point near a pH of 4.5. However, the pH did not remain stable when the titration was stopped but rose slowly. More acid was added; the pH again dropped to 4.5 but then rose slowly again. Several repetitions of this occurred until the effect disappeared and a stable end point was reached.

The best explanation of this behavior seems to be that the bicarbonate present as the complex MnHCO_3^+ ion reacts more slowly with H^+ than the HCO_3^- ion does. Hence, a residue of complexed bicarbonate is left after the uncomplexed ions have been titrated. As these complex ions react slowly with H^+ , they cause the pH to rise, but are ultimately all converted to Mn^{+2} and H_2CO_3 (aq) at a pH of 4.5. When a stable pH of 4.5 was reached, the solution retained no buffering capacity.

The behavior of the solutions during the alkalinity titration is a qualitative indication that complexing of part of the manganese takes place. No quantitative conclusions are justified from this evidence, however.

CALCULATION OF FREE ENERGY OF THE COMPLEX

A value for the standard free energy of formation of the complex can be calculated from the equilibrium constant for the reaction



and from data in tables 1 and 4. The net change in standard free energy in the reaction is related to the equilibrium constant by the equation

$$\Delta F^0 = -RT \ln K.$$

On substituting numerical values for R and T and converting to base -10 logarithms, this becomes $\Delta F^0 = -\log K(1.364)$. The free energy of formation of the complex is

$$\Delta F^0_{\text{Mn}^{+2}} + \Delta F^0_{\text{HCO}_3^-} - 1.364 \log K = \Delta F^0_{\text{MnHCO}_3^+}$$

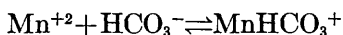
For the range of values of the equilibrium constant, the standard free energy of formation of the complex ranges from -196.9 to -197.3 kg-cal.

EFFECT OF THE COMPLEX ON MANGANESE EQUILIBRIA

Experimental evidence obtained in this work regarding bicarbonate complexing may be summarized as follows:

1. A complex cation assumed to have the formula MnHCO_3^+ increases the solubility of manganese in solutions containing an excess of dissolved carbonate species.

2. Reactions involving the bicarbonate part of the MnHCO_3^+ complex are slower than reactions of uncomplexed bicarbonate.
3. The equilibrium constant for the reaction



is 63, and the standard free energy of formation of the complex is $-197.1(\pm .2)\text{kg-cal}$.

4. In natural water containing an activity of 940 ppm of bicarbonate, half of any manganese present would be complexed. Thus the total solubility of manganese might be double that expected if complexing was not considered.
5. Bicarbonate complexing increases the solubility of manganese in natural water. When unusually large amounts of bicarbonate are present, the increase in solubility may be substantial.

Experiments reported by Listova (1959) indicate a somewhat greater solubility for manganese carbonate than the present work indicates. The solid formed in Listova's experiments was described as rhodochrosite but was in a finely divided state. Its behavior was more like the precipitated MnCO_3 used in this study than like the natural crystalline rhodochrosite described in the work of Garrels, Thompson, and Siever (1960). Data published by Listova are insufficient for calculation of free energies.

STABILITY FIELD OF BICARBONATE COMPLEX

Figure 6 represents a system similar to that of figure 2, except that activity of carbonate species is assumed to be 2,000 ppm in terms of HCO_3^- . Under these circumstances, most of the dissolved manganese is complexed when the pH is favorable. The equilibrium constant indicates that the ratio $[\text{MnHCO}_3^+]:[\text{Mn}^{+2}]$ actually has a value of a little more than 2, so that complexing is about two-thirds complete. The total solubility of manganese in the system is the sum of the solubilities of complexed and uncomplexed ions.

The stability boundaries that are calculated from equilibria in which bicarbonate-species activities are not involved are the same in both figure 2 and figure 6. Boundaries between fields of the oxides are identical in both diagrams.

The principal effect of increased activity of bicarbonate species is to enlarge the MnCO_3 (c) (rhodochrosite) field and to add a new field in which the complex MnHCO_3^+ is the dominant form. The MnCO_3 (c) field is enlarged at the expense of the area occupied in figure 5 by the solids Mn_2O_3 , Mn_3O_4 , and $\text{Mn}(\text{OH})_2$.

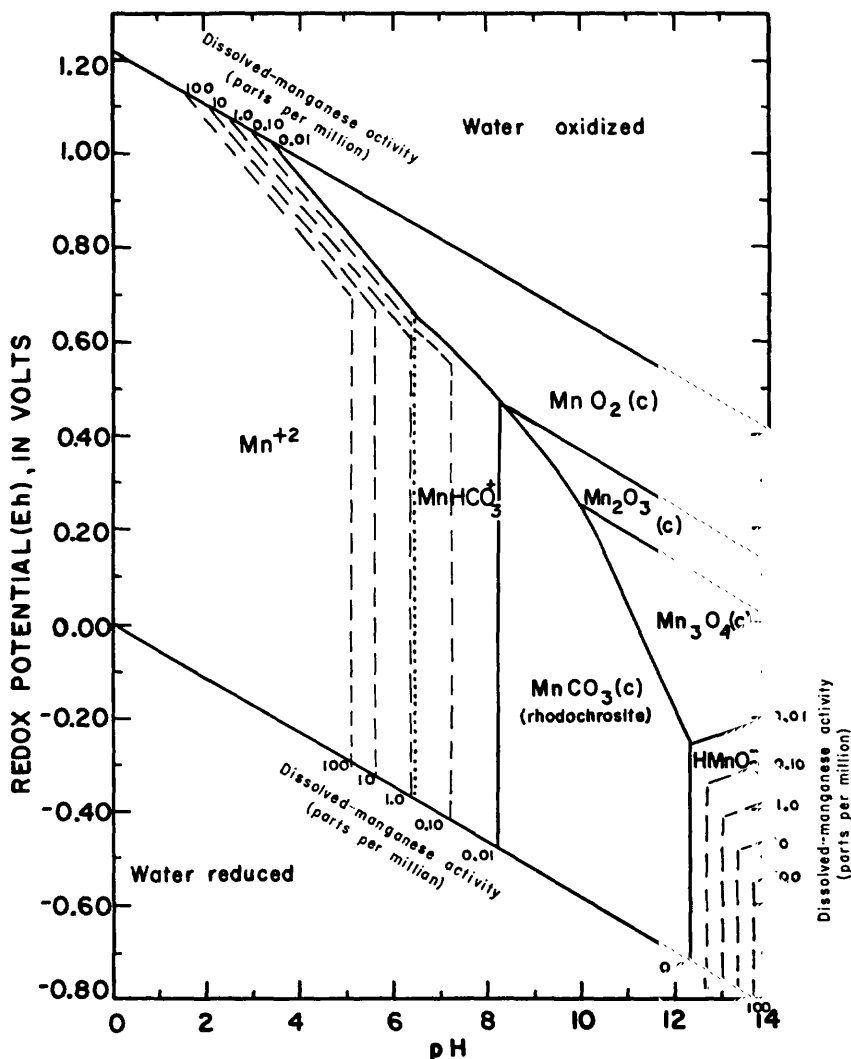


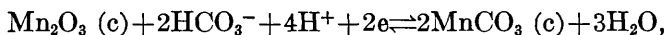
FIGURE 6.—Stability fields of manganese species in aqueous solution. Total dissolved manganese activity ranges from 0.01 to 100 ppm. Bicarbonate species activity is 2,000 ppm as HCO_3^- . Symbol (c) indicates crystalline form.

No $\text{Mn}(\text{OH})_2$ (c) stability field exists in figure 6, owing to the expansion of the MnCO_3 (c) field. In the HMnO_2^- area, the activity of dissolved manganese is governed by the equilibrium



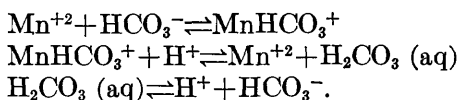
for which the value of K is 6.2×10^{-46} and by the redox equilibrium involving HMnO_2^- and Mn_3O_4 (c) used in previous diagrams.

Some of the boundaries of the MnCO_3 (c) field were computed from the same equations used in preparing figure 2, but larger values for HCO_3^- activity were used in the computations. The MnCO_3 (c) and Mn_2O_3 (c) fields did not touch each other in figure 2, however, and for their common boundary in figure 6 in the equilibrium applied was



where $E^\circ = 1.53$ v.

The stability field of MnHCO_3^+ is controlled by a new series of equilibria. The boundary along which the complex breaks down to form Mn^{+2} and HCO_3^- or H_2CO_3 (aq) is a function of pH. The equilibria governing concentrations along this boundary are:



Equilibrium constants for the reactions are given in table 2. The mathematical relationships that apply are:

$$\begin{aligned}\frac{[\text{MnHCO}_3^+]}{[\text{Mn}^{+2}][\text{HCO}_3^-]} &= 6.3 \times 10^1 \\ \frac{[\text{HCO}_3^-][\text{H}^+]}{\text{H}_2\text{CO}_3} &= 4.16 \times 10^{-7} \\ \frac{[\text{Mn}^{+2}][\text{H}_2\text{CO}_3]}{[\text{MnHCO}_3^+][\text{H}^+]} &= 4.2 \times 10^4.\end{aligned}$$

Also, because the total activity of the bicarbonate species is fixed and the activity of CO_3^{-2} and OH^- is negligible,

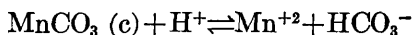
$$[\text{HCO}_3^-] + [\text{H}_2\text{CO}_3] = 3.28 \times 10^{-2}$$

and, because the activities of complexed and uncomplexed manganese are equal along the boundary,

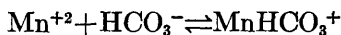
$$[\text{Mn}^{+2}] = [\text{MnHCO}_3^+].$$

These five equations can be solved simultaneously to give the pH at which the left boundary for the stability field of the complex should be drawn. The value obtained for the pH at the Mn^{+2} - MnHCO_3^+ boundary is 6.35. This boundary is represented by a dotted line on the diagram and is independent of the total manganese concentration, provided that a large excess of uncomplexed bicarbonate remains present.

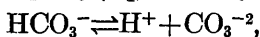
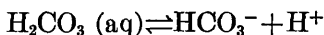
The vertical segment of the boundary between MnCO_3 (c) and MnHCO_3^+ is established from four equilibria:



where $K=0.31$



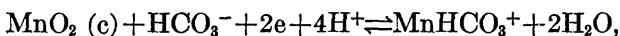
where $K=63$



and the known conditions at the boundary

$$\begin{aligned} [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{-2}] &= 3.28 \times 10^{-2} \\ [\text{Mn}^{+2}] + [\text{MnHCO}_3^+] &= 1.8 \times 10^{-7}. \end{aligned}$$

Actually, because the boundary is in the pH range where HCO_3^- is strongly dominant, it is sufficiently accurate to set the activity of HCO_3^- equal to 3.28×10^{-2} molal. The number of equations required to find the equilibrium pH is thus decreased. The value of pH for the boundary was found to be 8.2. The boundary between the MnHCO_3^+ complex and MnO_2 (c) was determined from the redox equilibrium



where

$$E^0 = 1.28 \text{ v},$$

and the first dissociation of carbonic acid. The amount of HCO_3^- available decreases with pH, and the slope of the boundary therefore changes below a pH of 7.0.

Some Mn^{+2} is in equilibrium with the complex and the total solubility of manganese can be computed from this equilibrium and the Nernst equation if the activity of the complex is taken as $\Sigma[\text{Mn}] - [\text{Mn}^{+2}]$.

The stability-field diagrams show some of the effects of changes in bicarbonate activity and complexing. In figure 2, the equilibrium activity of Mn^{+2} in the presence of rhodochrosite and 100-ppm HCO_3^- species is 0.10 ppm at a pH of 8.0. In figure 5, the activity of Mn^{+2} is about 1.0 ppm at this pH, owing to the decrease of HCO_3^- species to 10 ppm. In figure 6, a system containing 2,000 ppm HCO_3^- species activity is considered. If there were no complexing in this solution, manganese activity would be expected to be less than 0.01

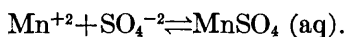
ppm at a pH of 8.0. Actually, the manganese activity at a pH of 8.0 is considerably greater than 0.01 ppm, as shown in figure 6. Because activity coefficients would decrease as concentration increased, the manganese concentration that would be measured in a system corresponding to figure 6 would be nearly double the activity.

The solubility of the oxides is increased a little by complexing, as shown by the "bulge" in the oxide boundaries in the stability field of the complex.

In figure 6, as well as in the other stability-field diagrams, it is assumed that anions containing C^{+4} , such as carbonate and bicarbonate, are stable in strongly reducing systems. Actually, organic forms of carbon theoretically would be the stable varieties in most of the reduced-sulfur region. The redox reactions of carbon are not readily reversible and have been omitted from consideration here.

MANGANESE SULFATE ION PAIR

Bjerrum, Schwarzenbach, and Sillén (1958) report an equilibrium constant of 1.9×10^2 for the reaction



This suggests that sulfate complexed with manganese is stable enough to be important in natural water. In a solution where activity of sulfate ions is 2,000 ppm (2.1×10^{-2} molal), about 80 percent of the manganese would be complexed.

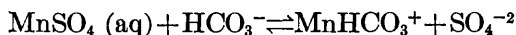
$$\frac{[MnSO_4]}{[Mn^{+2}][SO_4^{-2}]} = 1.9 \times 10^2$$

$$\frac{[MnSO_4]}{[Mn^{+2}]} = 1.9 \times 10^2 \times 2.1 \times 10^{-2} = 4.$$

A water that had a concentration of 2,000 ppm of sulfate would have an ionic strength of considerably more than 0.06, and the activity of sulfate would be substantially less than 2,000 ppm under these conditions.

COMPARISON OF STRENGTH OF COMPLEXES

Figure 7 compares the strength of the bicarbonate and sulfate complexes and indicates the degree of complexing to be expected when both HCO_3^- and SO_4^{-2} are present. The diagonal dashed line on the diagram is based on the equilibrium



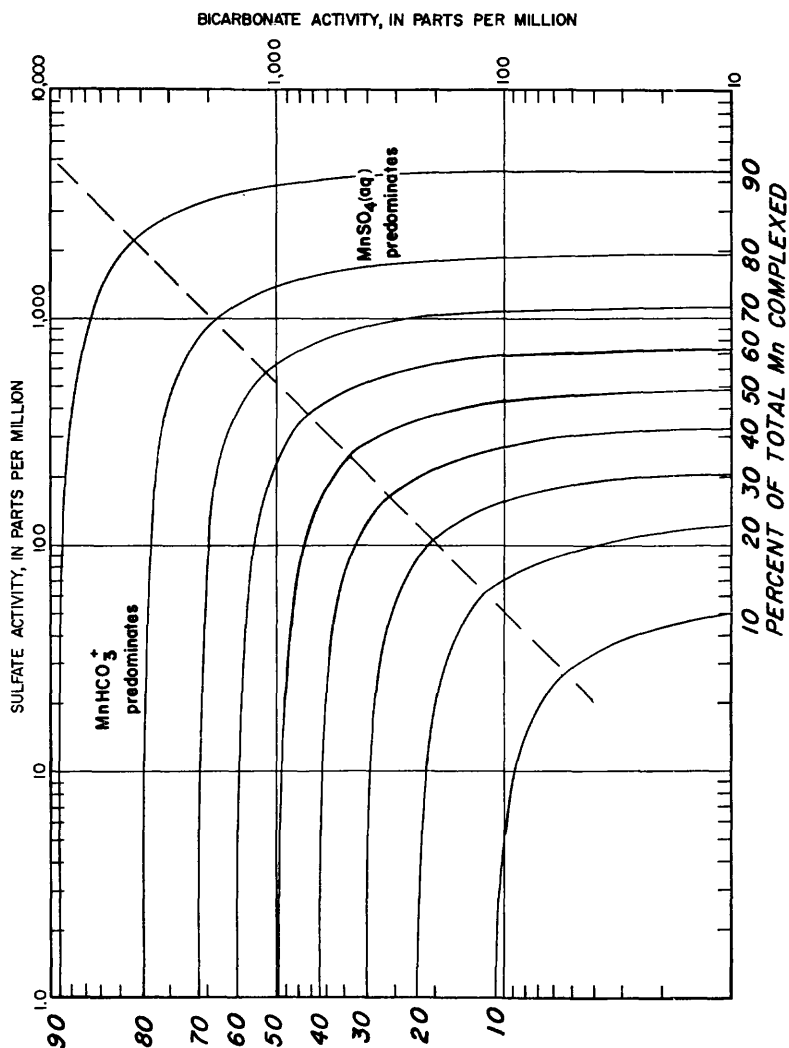


FIGURE 7.—Percentage of dissolved manganese present as complexes and predominant complex at different sulfate and bicarbonate activities. Symbol (aq) indicates aqueous solution.

for which the equilibrium constant is 0.32. When the activities of the complexes are equal,

$$[\text{SO}_4^{-2}] = 0.32[\text{HCO}_3^{-}].$$

The diagonal line based on this equation separates the area in which the sulfate complex would be the dominant form from the area where the bicarbonate complex would be dominant. Lines parallel to this line could be plotted for any desired value of the ratio $[\text{MnHCO}_3^{+}] : [\text{MnSO}_4(\text{aq})]$.

If it is assumed that the total activity of manganese in solution is the sum of the activities of Mn^{+2} , MnHCO_3^{+} , and $\text{MnSO}_4(\text{aq})$ and that the amount of manganese involved is small enough that the bicarbonate or sulfate combined with it does not significantly affect the supply of the anions, the ratios of the total activity of manganese species in solution to the total of the two complexes can be readily calculated. The results of these calculations are shown in figure 7 as contours that permit estimation of the proportion of manganese present as a complex when the activities of bicarbonate and sulfate are known.

The positions of the contours were calculated in two steps. First, parallel lines were drawn on the diagram for the following values of the ratio

$$[\text{MnHCO}_3^{+}] : [\text{MnSO}_4(\text{aq})] :$$

1/100, 1/10, 1/2, 1/1, 2/1, 10/1 and 100/1. The intersection of these lines with those for the activity of HCO_3^{-} or SO_4^{-2} that would give any selected percentage of complexing was then computed. For example, when the ratio

$$\frac{[\text{MnHCO}_3^{+}]}{[\text{MnSO}_4(\text{aq})]} = 1$$

and the manganese is 90 percent complexed, the three species are present in the ratio $[\text{Mn}^{+2}] = 10$, $[\text{MnHCO}_3^{+}] = 45$, and $[\text{MnSO}_4(\text{aq})] = 45$. In the equation

$$\frac{[\text{MnHCO}_3^{+}]}{[\text{Mn}^{+2}]} = 63[\text{HCO}_3^{-}]$$

the ratio on the left can now be determined as 4.5, and the value for $[\text{HCO}_3^{-}]$ as 7.14×10^{-2} molal, or 4,360 ppm. Similar calculations for each of the other values for the ratio of the complexes gives a series of points to which a curve is fitted to represent 90 percent complexing.

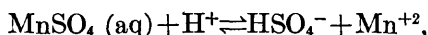
Figure 7 is based on activities and is directly applicable only to solutions with a rather small manganese concentration. However, the usual manganese concentration in natural water is less than 1.0 ppm; and when suitable activity corrections are calculated, the graph will give useful indications of the state of manganese dissolved in natural water. Obviously, in many of these solutions, 25 percent or more of the dissolved manganese occurs as a complex. The complexed manganese can be expected to behave differently in chemical equilibria than does uncomplexed manganese. The complexes probably will also react at rates different from those of uncomplexed manganese ions.

COMBINED EFFECTS OF BICARBONATE AND SULFATE COMPLEXES ON MANGANESE EQUILIBRIA

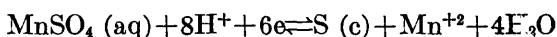
Figure 8 represents a system in which sulfur-species activity is 2,000 ppm in terms of sulfate and bicarbonate-species activity is 2,000 ppm as HCO_3^- (same as in figure 6). The increased availability of sulfate is sufficient to complex manganese in a considerable part of the diagram. The stability field for MnHCO_3^+ is confined to the reducing region, because the sulfate complex would predominate when SO_4^{2-} and HCO_3^- activities are 2,000 ppm.

The boundaries of the MnSO_4 (aq) field were determined from equilibrium constants and standard potentials.

For the Mn^{+2} - MnSO_4 (aq) boundary, the data needed are:

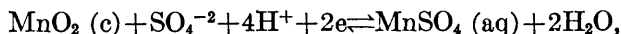


where $K=4.6 \times 10^{-1}$;



where $E^0=0.335$ v; and similar redox equilibria for reduction to H_2S and HS^- .

For the MnSO_4 (aq)- MnO_2 (c) boundary, below a pH of 6.4,



where $E^0=1.291$ v. This activity of MnSO_4 (aq) in the area of dominance of the complex is 80 percent of the total manganese activity, and therefore the value for $[\text{MnSO}_4]$ used in computing the boundary is taken as $0.01 \text{ ppm} \times 0.80$ or 1.46×10^{-7} molar.

Both the sulfate and the bicarbonate complexes affect the area of figure 8 that coincides with the area occupied by the bicarbonate complex in figure 6. The total activity of manganese in this area is

$$\Sigma[\text{Mn}] = [\text{Mn}^{+2}] + [\text{MnHCO}_3^+] + [\text{MnSO}_4].$$

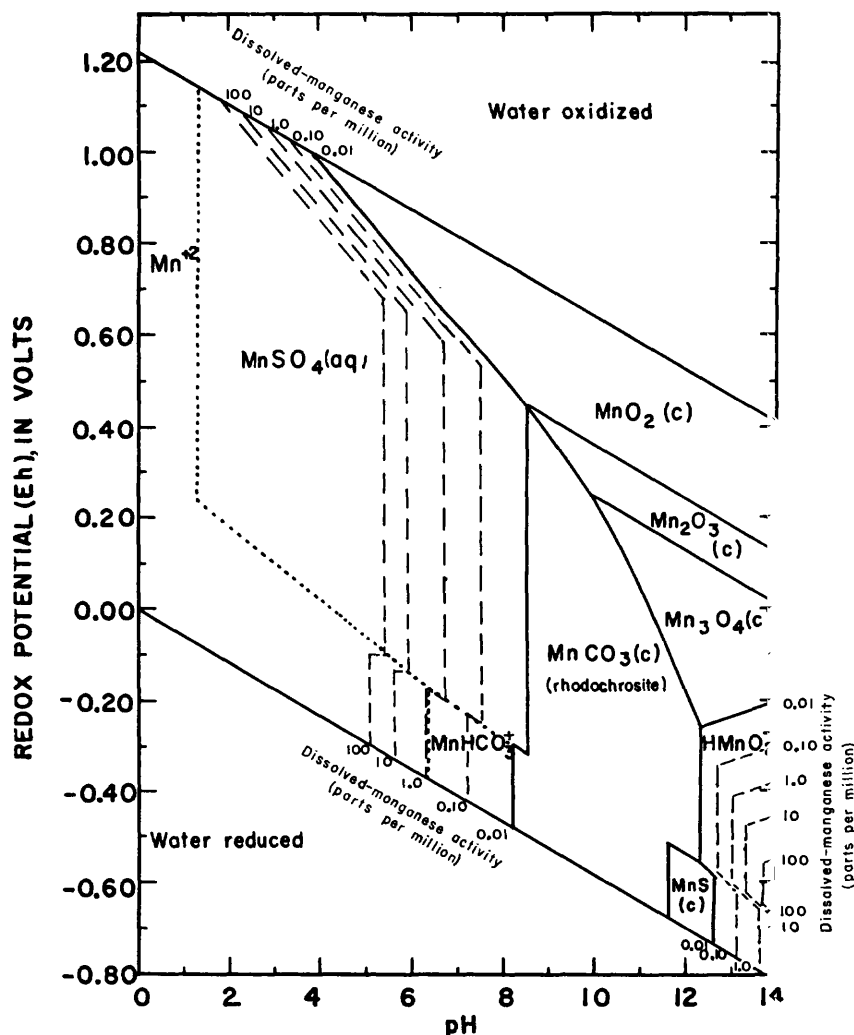
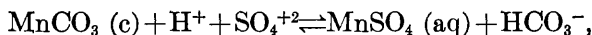


FIGURE 8.—Stability fields of manganese species in aqueous solution. Manganese activity ranges from 0.01 to 100 ppm; bicarbonate-species activity is 2,000 ppm as HCO_3^- ; and sulfur-species activity is 2,000 ppm as SO_4^{+2} . Symbol (c) indicates crystalline form and (aq) aqueous solution.

The relative amounts of the three species are in the ratio 1 to 2.1 to 4, where all the 2,000 ppm of bicarbonate species are present as HCO_3^- .

To compute the position of the MnCO_3 (c)- MnSO_4 (aq) boundary for 0.01 ppm total dissolved manganese activity, a good approximation can be obtained from the equilibrium



where $K=55$.

The total manganese activity is 1.8×10^{-7} molal, and the fraction of the total activity due to MnSO_4 (aq) is

$$\frac{[\text{MnSO}_4]}{[\text{MnSO}_4] + [\text{Mn}^{+2}] + [\text{MnHCO}_3^+]} = \frac{4}{7.1}.$$

Multiplying

$$[\text{MnSO}_4] = \frac{4}{7.1} \times 1.8 \times 10^{-7},$$

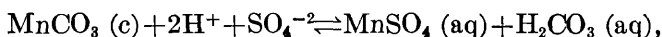
or

$$[\text{MnSO}_4] = 1.01 \times 10^{-7} \text{ molal.}$$

The computation gives a pH of 8.5 for the boundary. When the total manganese activity is increased to 1.8×10^{-6} molal, the pH is 7.5.

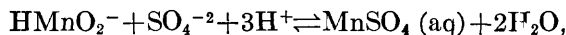
Further increases in total manganese activity require a change in the fundamental equations. When manganese activity is 1.0 ppm, the pH evidently will be near the edge of the MnHCO_3^+ field, so that activities of the uncomplexed Mn^{+2} and the MnHCO_3^+ will be about the same. The ratio of species will then be 1 to 1 to 4 and the molal MnSO_4 (aq) activity will be $\frac{1.8 \times 10^{-5} \times 4}{6}$. Also, the bicarbonate activity will be only about half the total at pH 8.5, or about 1.6×10^{-2} molal. Substituting these values in the equilibrium expression gives a pH of 6.7 for the 1.0-ppm-manganese activity line.

The positions of the 10- and 100-ppm lines were computed from the equilibrium



where $K = 1.28 \times 10^8$, and the assumption that the MnSO_4 (aq) activity is four-fifths of the total activity of dissolved manganese species in this region.

From the equilibrium



for which the value of K is 4.1×10^{36} , it follows that the MnSO_4 (aq) form will not predominate above a pH of 11.6 when SO_4^{-2} and CO_3^{-2} activities are at the levels postulated.

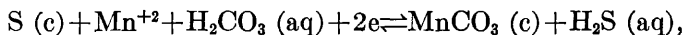
Equilibria that were used to locate the boundaries of the MnS (c) field are the same as those in figure 5, except for the vertical segment of the MnCO_3 (c)- MnS (c) boundary. This is calculated from the equilibrium



for which the value of K is 3.5×10^{-12} .

The dashed lines in the HMnO_2^- field are the same as those in that area in figure 6, except where they are affected by equilibria involving MnS (c).

When sulfate ions are reduced, free sulfur is a possible stable variety. Therefore, the equilibrium



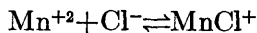
where $E^0 = -0.239$ v, was considered in locating the dashed lines of dissolved manganese species below a pH of 6.0. This relation is independent of pH and gives rise to short horizontal segments in the lines for dissolved-manganese activities of 10 and 100 ppm.

The effects of sulfate complexing are plainly indicated in figure 8. In the area where $\text{MnSO}_4 \text{ (aq)}$ is dominant, the lines representing dissolved-manganese activity are each displaced about 0.3 pH unit to the right, as compared with their positions in the MnHCO_3^- and Mn^{+2} areas.

Mah (1960) gives the free energy of formation of two manganous silicates, MnSiO_3 and Mn_2SiO_4 . No computations have been attempted with these, however. Figure 8 shows about as many variables as can usefully be shown on a single diagram, and the silicates of manganese in nature are generally not simple enough to be represented by the compounds for which thermodynamic data are available.

OTHER INORGANIC COMPLEXES

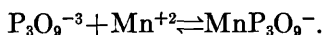
The chloride complexes with divalent manganese evidently are rather weak, although relatively little information seems to have been obtained about them. Kraus and Moore (1953) found that anionic complexes of manganese and chloride, with a coordination number of 6, such as of the type MnCl_3^- and MnCl_4^{2-} , are not formed in detectable amounts unless the chloride concentration exceeds about 4 molal. According to Bjerrum, Schwarzenbach, and Sillén (1958) J. C. James reported in 1947 that the value of K for the equilibrium



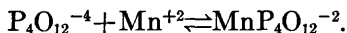
is only about 1. For half the manganese to be complexed, the chloride activity would thus need to be about 1 molal, or some 35,000 ppm. This chloride value is attained only in brines. This discussion is centered on the more dilute kinds of natural water, and therefore the chloride complexes are not given further consideration here.

Phosphate ions can form strong complexes with manganese. Bjerrum, Schwarzenbach, and Sillén (1958) quote Jones, Mork, and

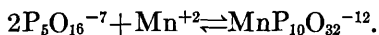
Davies (1949) who report a constant of 3.7×10^3 for the equilibrium



The same publication quotes Jones and Monk (1950), who found a constant of 5.5×10^5 for the equilibrium



Also, Van Wazer and Campanella (1950) reported a constant of 3×10^5 for the equilibrium



Apparently, only a few parts per million of polyphosphate in solution should serve to complex most of any small amount of manganese that may be present. Complexing of manganese by orthophosphate and pyrophosphate is reported to be either weak or to be nonexistent by several investigators quoted by Bjerrum, Schwarzenbach, and Sillén.

Natural water usually does not contain phosphate in amounts sufficient to complex manganese. In treatment processes, however, polyphosphates are rather widely used to delay or to prevent precipitation of calcium carbonate or iron or manganese oxide or hydroxide. Polyphosphate anions are not stable in water and slowly change to orthophosphate; hence, the effects of adding polyphosphate are only temporary.

Rather large amounts of phosphate are required for complete complexing of calcium and magnesium, which are major dissolved constituents in water. A considerable effect on the behavior of calcium can be observed from an amount of polyphosphate that is not nearly large enough to complex all the calcium. The retarding of calcium carbonate precipitation that results from small amounts of polyphosphate is termed the "threshold effect." It is generally attributed to dispersion of the small aggregates of CaCO_3 as they form in the solution, so that the particles do not grow large enough to precipitate.

Manganese and iron are minor constituents in most waters. Illig (1957, 1960) stated that the amounts of polyphosphate needed to control the precipitation of manganese are considerably in excess of the amount of manganese in solution, which suggests that a complexing effect is the principal one involved. The complex is destroyed both by oxidation of manganese and by degradation of the polyphosphate to form orthophosphate.

Phosphate generally constitutes a considerable part of household detergents. Water polluted by domestic or industrial sewage can be expected to contain phosphates from this and other sources.

ORGANIC COMPLEXES

Soluble organic complexes containing iron were studied by Shapiro (1958). The writer (Hem, 1960b) found that ferrous iron formed a soluble complex with tannic acid and that the complexed iron is more slowly oxidized than the uncomplexed form. This feature of the chemistry of iron is at least locally important because the usual conditions to which surface water is exposed result in almost immediate oxidation of uncomplexed ferrous iron to the nearly insoluble ferric iron. The complexing action permits ferrous iron to be carried considerable distances in solution in streams or in soil and subsoil moisture.

Enough evidence of the behavior of manganese already has been presented to show that small amounts of manganese can be stable in a soluble form in most surface water, either as Mn^{+2} or as bicarbonate or sulfate complexes. Media that could transport manganese in the reduced soluble form are commonly present and organic complexing is not essential for such transport. Nevertheless, published literature ascribes certain features of manganese behavior to organic complexes, and some work was done to see if a tannic acid-manganese complex could be formed.

A solution containing 10 ppm Mn^{+2} and 500 ppm tannic acid was prepared, together with a similar tannic acid solution containing no manganese. Aliquots of these solutions were raised to selected levels of pH by adding sodium hydroxide solution, and their percentage transmittance was measured by use of a Beckman model-B spectrophotometer over the wave-length range 400 to 650 m μ . The resulting curves of transmittance plotted against wavelength were similar for the two solutions below a pH of 5. At a higher pH the solutions had a deeper color, but the shapes of the transmittance wave-length curves remained about the same; apparently, no distinctively colored complex was formed.

At a pH of 7.0, the manganese tannic acid mixture had a pronounced greenish color. This solution grew darker slowly on standing, although the rate of change became almost imperceptible after an hour or so. The corresponding tannic acid solution at a pH of 7.0 (no manganese present) also had a greenish color, but at first it was a paler shade than the solution containing manganese. As time passed, the color of the tannic acid solution deepened. Apparently, most of the change of color in the solutions was a result of changes in the tannic acid as the pH was raised. Manganese seemed to accelerate these changes.

A solution of tannic acid and manganese raised to a pH of 8.5 contained a small amount of finely divided black material that may have been a colloidal dispersion of a tannic acid- Mn^{+4} complex similar

to the black material formed by tannic acid in combination with ferric iron.

The results of these experiments suggest that manganese could be present as a constituent of organic coloring matter in surface waters, although no well-defined complex of tannic acid and divalent manganese is indicated. Colloidal suspensions of manganese oxides, however, may be stabilized by organic matter at pH levels near neutrality or in the alkaline range.

The behavior of mixtures of tannic acid and Mn^{+2} was studied further by mixing tannic acid solutions of concentrations from 5 to 500 ppm with manganese stock solution, adjusting the pH, and observing changes in concentration of manganese while the solutions were standing in contact with air over a period of 3 weeks. Some of the solutions retained some manganese that passed through a plastic-membrane filter whose (pore diameter was 0.45μ) at pH as high as 10 for the entire 3 weeks. However, some of this manganese may have been colloidal particles of oxide.

Because the tannic acid molecule is about six times as heavy as the Mn^{+2} ion, a 1 to 1 complex requires a ratio of 6 ppm of tannic acid to 1 ppm of manganese. Thus, complete complexing of 10 ppm Mn^{+2} would not occur in solutions containing less than about 60 ppm tannic acid. Apparent effects on the oxidation of manganese in the presence of 5.0 and 50 ppm concentrations of tannic acid were noted, however. These may result from the reducing effect of tannic acid.

Complexes of manganese with many different organic ions are cited by Bjerrum, Schwarzenbach and Sillén (1957). In general, the stability constants for ferrous and manganous complexes with the same organic ligand show that the ferrous complexes are stronger. The behavior of manganese with tannic acid solutions observed in this study, seems to agree with this general observation. Irving and Williams (1953) reported that several complexes containing manganese were less stable than similar complexes containing 5 other transition metals, including iron.

RATES OF CHEMICAL REACTION

Thermodynamic calculations such as those made in preparing figures 1-8 require that the evaluated systems be in a state of chemical equilibrium. Whether equilibrium actually is attained in a system depends on the rates of the various chemical reactions that may take place and on the length of time that the reacting substances and products remain undisturbed in contact with one another. Reaction rates are affected by concentrations of reactants and products, by temperature, and by the action of catalysts; but they are not readily

predicted on theoretical grounds and must generally be determined by experiment. A convenient measure of reaction rate is the "half-life" time, the length of time in which half the reacting substances present at the beginning of this period of time are converted to products.

Whether a given reaction rate is "fast" or "slow" depends on the point of view of the individual. In analytical chemistry the most useful reactions have short half lives, preferably not more than a few seconds. The reactions of value in industrial chemistry may be slower, but for most processes a half-life time greater than an hour or so would be excessive.

Although man's manipulation of chemical processes emphasizes rapid reactions, in nature the pace can be much more leisurely. In geochemical processes, such as ore deposition or metamorphic alteration of rock minerals, reactants and products may remain in undisturbed contact for many thousands of years; hence, equilibrium can be reached even in very slow reactions. Natural processes that take place in surface-water bodies or in ground water near the land surface, however, are subject to fluctuations in temperature and pressure. Because the solutions generally are in motion, whereas the solids are stationary, or move at a slow rate, the time available for equilibrium to be established is ordinarily not long in the geologic sense. In surface-water systems, a reaction whose half-life time is a few hours will generally reach equilibrium; and in ground-water systems, a reaction whose half-life time is many days, or even a few years, can generally be expected to reach equilibrium.

Some knowledge of the rates of reaction of manganese is essential, so that one may know the extent to which thermodynamic calculations can be applied. Obviously, such calculations have little practical usefulness if equilibrium cannot be expected to be reached in nature. Approximate indications of rate will suffice for this purpose. A closer determination of reaction rates for oxidation of Mn^{+2} in aerated water and the effects of other ions on the rate is of considerable practical value as this reaction is important in water treatment.

KINETICS OF MANGANESE OXIDATION AND PRECIPITATION

No data on the kinetics of oxidation of Mn^{+2} to Mn^{+3} and Mn^{+4} in aerated solutions resembling natural water could be found in published literature. The general features of similar oxidation reactions such as those involving iron may give some indication of what should be expected. Stumm and Lee (1961) studied the oxidation of ferrous iron in aerated water containing bicarbonate and carbonate ions. They concluded that the oxidation reaction is first-order with respect to ferrous-iron content and that the rate is strongly influenced by pH.

An increase of 1 pH unit brought about a 100-fold increase in oxidation rate.

Manganese oxidation reactions are likely to be more complicated than the ones for ferrous iron, because manganese can be oxidized to the Mn^{+3} or Mn^{+4} states. The bicarbonate and sulfate complexes of reduced manganese can also be expected to affect the reaction rate.

In earlier experiments the oxidation of manganese was accompanied by a rise in H^+ activity. A series of titrations was made in an effort to evaluate this effect and to see if an indication of reaction rate as affected by pH could be obtained. Distilled-water samples containing 2.0 mg of Mn^{+2} were prepared and were raised to a previously selected pH by rapid addition of 0.01*N* KOH from a burette. The solution was maintained at a constant pH by additions of the standard base, and the burette readings were plotted against elapsed time. The results obtained at a pH of 8.0, 8.5, and 9.0 are given in figure 9.

The oxidation and precipitation at a pH of 9.0 occurred rapidly and appeared to be complete in about 5 minutes. At lower pH, the reaction was much slower and did not appear to reach a definite end point. The amount of base consumed was also greater at lower pH. No quantitative interpretation of the results in figure 9 is possible. Evidently, the products of the reaction change as the pH changes, and the effects of carbon dioxide species on the titrations are difficult to evaluate. Air was not excluded from the samples, but the base used was free of carbonate.

To provide more specific data, a second series of titrations was made. In this series, the pH was held constant and samples were taken at intervals of a few minutes. The samples were filtered at once through a plastic membrane filter having a pore diameter of 0.45μ , and manganese content of the filtrate was determined. The results for solutions held at a pH of 8.5 and 9.0 are shown in figure 10.

Although the individual points are somewhat scattered, they give a fairly well defined linear relationship between log of dissolved manganese concentration and time and suggest that the oxidations at these two pH values are first order with respect to manganese concentration. The half-life time at a pH of 9.0 is about $1\frac{1}{2}$ minutes; and at a pH of 8.5, about 30 minutes.

Precautions were taken to exclude carbonate from the standard base used, but the solutions were open to the air during the titration. Effects of CO_2 introduced from this source probably were minor.

EFFECT OF SULFATE

The effect of sulfate on the rate of oxidation was studied in a series of titrations in which pH was held at 9.0, 9.2, and 9.5. The solutions used were prepared in the same way as in the preceding series, except

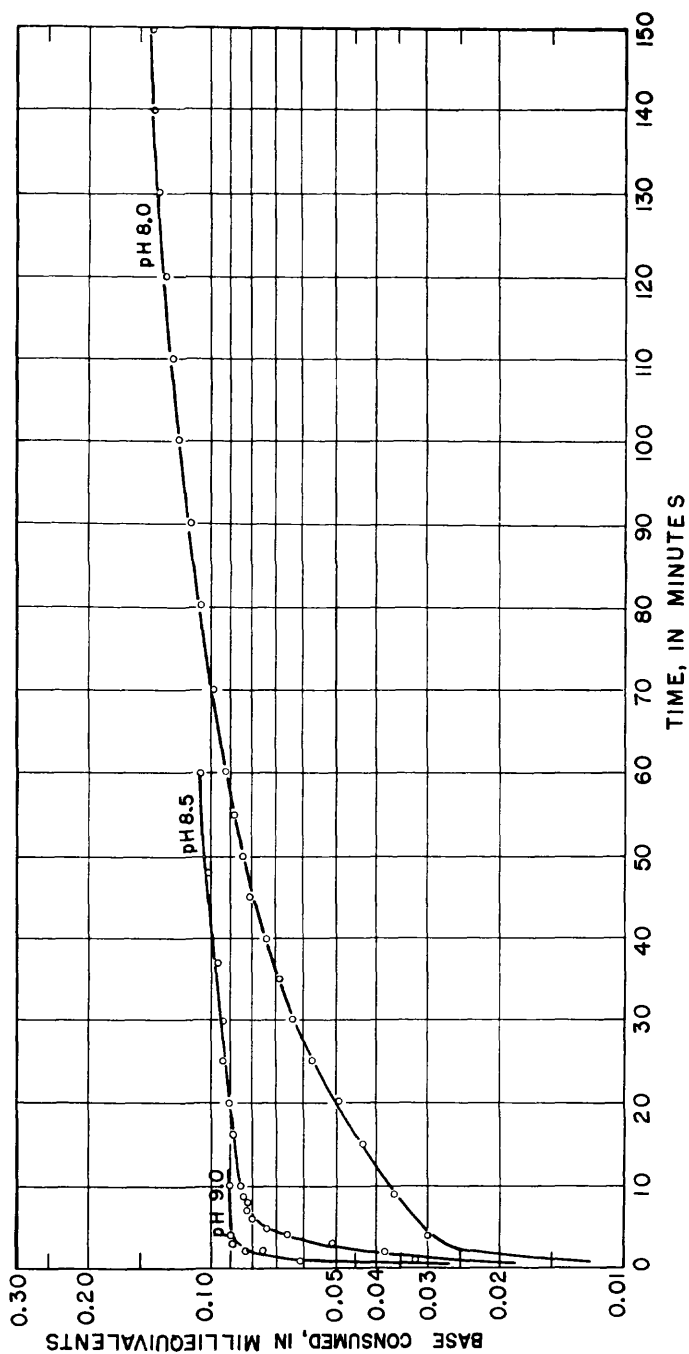


FIGURE 9.—Rate at which base KOH, was consumed to maintain constant pH in three solutions, each containing 2.0 milligrams Mn^{+2} initially. Bicarbonate and sulfate species were absent.

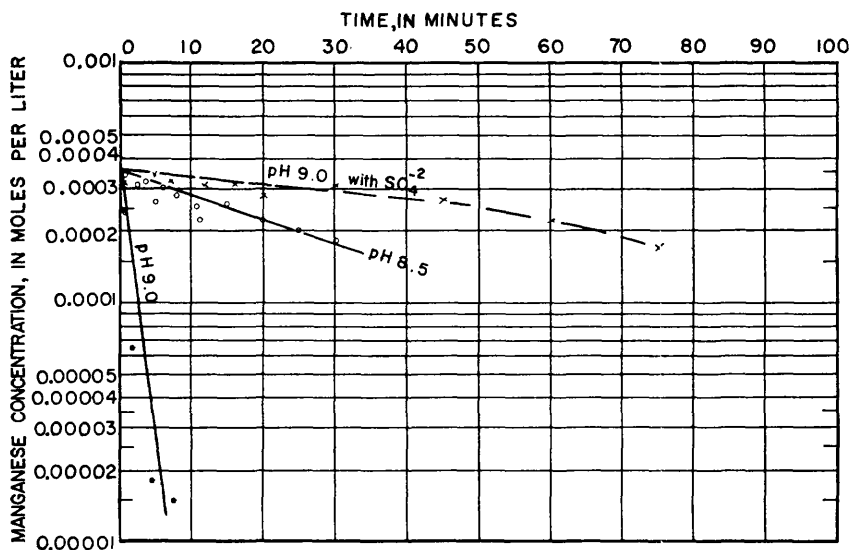


FIGURE 10.—Rate at which manganese was oxidized at a pH of 8.5 and 9.0 in the absence of sulfate, and at a pH of 9.0 with a sulfate concentration of 2,000 ppm.

that sodium sulfate was added to give a concentration of 2,000 ppm SO_4^{-2} . Samples were withdrawn for manganese determination at various time intervals. Results obtained at pH 9.0 are shown in figure 10.

The relationship between $\log C_{\text{Mn}^{+2}}$ and time is approximately linear during the first hour, but the rate appears to increase somewhat thereafter. A similar effect was noted in later studies using solutions containing bicarbonate. Extrapolation of the initial rate shows that when pH is 9 the apparent oxidation half life is about 80 minutes in the presence of 2,000 ppm sulfate, compared to 1.5 minutes in the absence of sulfate. The presence of sulfate also slowed oxidation rates at a pH of 9.2 and 9.5, but no rates of oxidation at these pH levels for sulfate-free solutions are available. The effect of sulfate is undoubtedly related, at least in part, to the presence of MnSO_4 (aq) complex.

EFFECT OF BICARBONATE

A further series of experiments was made to determine the effects of bicarbonate ions on the rates at which manganese is oxidized and is precipitated. In this series, solutions containing 2.0 mg of Mn^{+2} in 100 ml of distilled water with 100 ppm of HCO_3^- present were prepared. The pH of these solutions was then raised to values near 9.0. The buffering effect of bicarbonate prevented the pH from changing rapidly as a result of the hydrolysis of oxidized manganese and permitted a somewhat closer control of pH than was

possible in the other experiments. During each titration, an aliquot was removed every few minutes and filtered through a plastic-membrane filter with a pore diameter of $0.45\ \mu$. The manganese concentration of each of the filtered aliquots was determined. Figure 11 is a graph in which the concentrations of manganese in solution are plotted against time elapsed after raising the pH. The pH of the three solutions represented in figure 11 was maintained at 9.0, 9.1 and 9.3.

Manganese remaining in solution, presumably as Mn^{+2} or MnHCO_3^+ , was measured directly in this experiment, and the results in figure 11 are comparable to those in figure 10.

Data in figure 11 show that the bicarbonate ions slowed the reactions by which manganese was precipitated at about the rate as the sulfate ions did. At a pH of 9.0, for example, the half-life time is about an hour when bicarbonate is present. In the absence of bicarbonate and sulfate, the half life was $1\frac{1}{2}$ minutes at this pH.

The half life at a pH of 9.0 in the presence of 2,000 ppm SO_4^{-2} was about 80 min. The results suggest that bicarbonate ions are somewhat more effective in slowing the oxidation than are sulfate ions.

The relationship of $\log C_{\text{Mn}^{+2}}$ and time was nearly linear for the first part of each of the titrations, which suggests that, at least at first, the oxidation at constant pH is a first-order reaction whose rate depends only on the amount of Mn^{+2} available. Rate constants for this part of the reaction could be calculated, but they would not represent an overall reaction rate.

As the reaction proceeds, the rate tends to increase; as shown by the changing slopes of the curves in figure 11. This suggests that the rate of manganese precipitation may be increased by autocatalysis—that is, self-catalysis by the oxide causes further oxidation and precipitation of manganese.

The effect of bicarbonate on the oxidation rate does not seem to be directly related to complexing, because only a small amount of complexing occurs when 100 ppm of bicarbonate is present. To obtain comparable rates in duplicate experiments where bicarbonate is supposedly absent requires considerable care to exclude atmospheric carbon dioxide from the standard base, and the base must be prepared from carbonate-free hydroxide. Small amounts of carbonate species introduced in the reagent have a very marked effect on the reaction rate.

FACTORS THAT MAY INCREASE REACTION RATE

Although the laboratory work with HCO_3^- and SO_4^{-2} ions showed that they retarded the rate of oxidation of manganese, other substances may increase the rate. Some micro-organisms can greatly

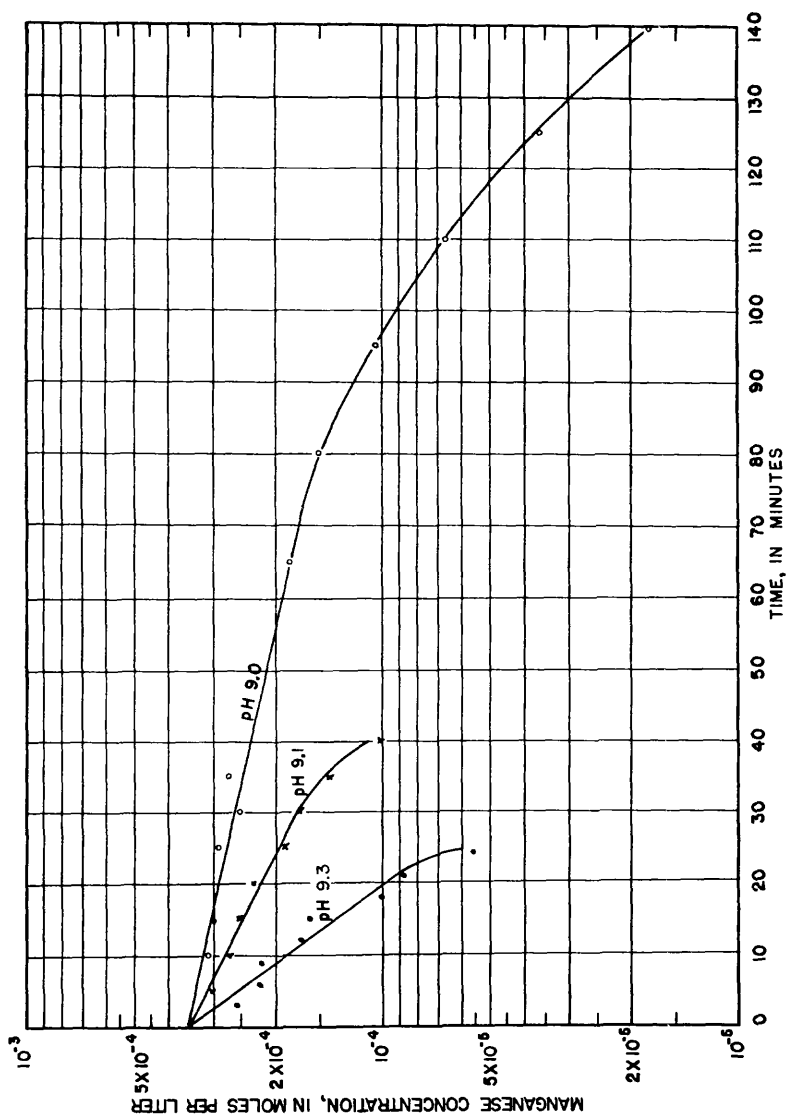


FIGURE 11.—Rate at which manganese was oxidized at three pH levels in the presence of 100 ppm HCO_3^-

increase the rate of oxidation of iron and others are known to be effective in catalyzing the oxidation of manganese.

Futral and Ingols (1953) reported that 0.5 ppm CuSO_4 that had been added to a water-supply reservoir speeded the removal of manganese from the water by oxidation. Small amounts of copper also catalyze the oxidation of ferrous iron. Dhar and Kishore (1950) reported that $\text{Mn}(\text{OH})_2$ was oxidized in the presence of other metal cations at a more rapid rate as pH was increased and that most of the other metallic hydroxides that were studied increased the rate. Some of the other metal hydroxides, however, had no effect and AgOH decreased the rate.

SUMMARY

The results of the rate experiments may be summarized as follows:

1. The rate at which manganese is oxidized and precipitated from aerated solutions is affected by pH and by other ions that may be present.
2. The rate is increased by raising the pH and is decreased by presence of HCO_3^- and SO_4^{2-} .
3. The rate at which manganese is precipitated by the oxidation effect of air is rapid enough to be of use in water treatment only at pH 9.5 or more unless the water is unusually pure or if the reaction is catalyzed.
4. Although the rate of oxidation of manganese is slower than that of iron, in ordinary ground-water systems the time required for circulation is generally long enough so that equilibrium is probably generally reached. However, some metastable reduced manganese could be transported for considerable distances in surface streams.
5. The rate experiments suggest that the chemical equilibrium needed for application of the stability-field diagram is likely to exist in most natural-water systems where a sufficient supply of manganese minerals is present.

COPRECIPITATION OF MANGANESE WITH FERRIC HYDROXIDE

In studies of the chemistry of iron, Hem and Skougstad (1960) found that when ferric hydroxide precipitated from solutions containing about half a part per million of copper, the copper also was removed when the pH of the solution was high enough. The critical level for pH was found to be about 5.5. Above this level of pH, appreciable amounts of copper were removed from solution by the precipitated ferric hydroxide.

Manganese and iron often occur together in natural water. If the water is subjected to mild oxidation or if the pH is raised, the relatively

unstable ferrous iron is likely to be oxidized and precipitated. Manganese should remain in solution while these processes are going on, however, unless rather strong oxidizing agents are present or the pH is very high, but there is a possibility of coprecipitation of manganese with the iron. This possibility was investigated in simple solutions containing ferrous iron that was being oxidized and from which $\text{Fe}(\text{OH})_3$ was precipitating. A series of solutions each containing 10 ppm Fe^{+2} and 10 ppm Mn^{+2} was prepared and their pH was raised to a selected level ranging from 6.0 to 8.0 in half-unit steps. The iron began to precipitate from all the solutions almost at once. The pH decreased slowly in each solution. After 3 days the pE^- , Eh, and the Fe^{+2} and Mn^{+2} contents of each solution were measured. This was repeated 10 days and 14 days after the start of the experiment. The results are given in table 5. A comparison of the results of the coprecipitation experiment with similar solutions containing no iron can be obtained by comparing tables 3 and 5.

Solutions 1-3 in table 3 and 3-5 in table 5 should be closely comparable. The solutions initially brought to a pH of 7.0 or 7.5 lost very little manganese in either experiment and attained about the same pH at the end of 3 to 5 days. The Eh of the samples containing manganese and iron, however, was considerably less at 3 days than that of the ones which contained only manganese after 5 days. The Eh values probably were affected by iron species.

TABLE 5.—*Coprecipitation of manganese with ferric hydroxide*

Solution	Time (hours)	Mn ⁺² concentration (ppm)	Fe ⁺² concentration (ppm)	pH	Eh (volts)
1-----	0	10	10	6.0	-----
	72	10	-----	6.2	0.24
	240	10	3.2	4.7	.47
	408	10	-----	4.7	.46
2-----	0	10	10	6.5	-----
	72	10	-----	6.5	.18
	240	10	.04	6.4	.40
	408	10	-----	6.1	.41
3-----	0	10	10	7.0	-----
	72	9.8	-----	6.7	.20
	240	9.5	.00	6.6	.39
	408	10	-----	6.2	.41
4-----	0	10	10	7.5	-----
	72	9.8	-----	6.8	.20
	240	9.2	.00	6.7	.39
	408	9.2	-----	6.3	.41
5-----	0	10	10	8.0	-----
	72	6.2	-----	6.9	.20
	240	5.8	.00	6.8	.39
	408	5.0	-----	6.4	.41

The samples initially brought to a pH of 8.0 provide a comparison of manganese behavior in the presence of iron with that when iron is absent. When iron was present, about 40 percent of the manganese was removed from solution after 3 days and 50 percent, after 17 days. When manganese was present alone, no important amount was lost from solution over a 5-day period.

The amount of manganese lost from solution at a pH of 8.0 probably resulted from some manganese being incorporated in the ferric hydroxide crystal lattice. The amount lost appears to be too large to be attributed to adsorption on the small amount of precipitate that was present. The loss between the 3-day and 17-day observations, however, could have been related to adsorption.

At a pH of 8.0 some direct oxidation of manganese could have occurred but this solution probably did not remain at that pH long enough for much of this to take place.

Some minor amounts of adsorption of manganese may have taken place at a pH of 6.7 or more.

In the work of the writer (Hem and Skougstad, 1960) with coprecipitation of copper, the critical pH above which copper ions were removed from solution by ferric hydroxide precipitates was near 5.5. Cupric ions are somewhat smaller than Mn^{+2} ions; hence, stronger adsorption effects would be expected for copper than for manganese. This agrees with the observation that manganese is not adsorbed until the pH reaches 6.7. The strength of negative charges on ferric hydroxide particles increases with increasing pH from the isoelectric point, which is reported by Krause (1928) to be 5.2.

Krauskopf (1957) has discussed the geochemical factors that may govern the separation of manganese from iron in sedimentary deposits.

COPRECIPITATION OF MANGANESE AND OTHER ELEMENTS

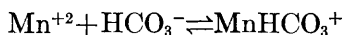
The literature contains many papers on the coprecipitation of manganese with other elements. Hikime (1954) reported that as much as 2 mg Mn^{+2} could be carried down on 100 mg of $Al(OH)_3$. The solutions used in these studies were relatively high in manganese content.

The precipitation of other elements with manganese oxides is evidently a common occurrence, as suggested by the abundant impurities in some types of manganese ores. The tendency for manganese oxide to adsorb cations is demonstrated by the composition of manganese-bearing nodules recovered from the floor of the Pacific Ocean. Goldberg (1954) found that the nickel and copper contents of manganese nodules was proportional to the manganese content.

GENERAL CONCLUSIONS

The general features of the chemical behavior of manganese in natural water and in the laboratory are in accord with chemical-equilibrium calculations. Reasonable agreement between laboratory data and calculated data was obtained in dilute solutions of Mn^{+2} in distilled water. The oxides produced, however, were not pure and some appeared to be hydrated.

In the presence of bicarbonate and sulfate anions and in the concentration range common in natural water, manganese displays a pronounced tendency to form complexes. These complexes can be an important factor in manganese chemistry. The equilibrium constant for the complexing reaction



was found to be 63. An uncharged ion pair, MnSO_4 (aq), which is reported in published literature to be somewhat more stable than the bicarbonate complex, is formed with sulfate. In the presence of an activity of 250 ppm of sulfate and 470 ppm of bicarbonate, and a total dissolved manganese activity not exceeding about 1.0 ppm, half of the manganese would be present in the form of complexes. Manganese may form strong complexes with phosphate and with some organic ions.

In general, the effects of Eh, pH, and commonly occurring anions in natural water are less restrictive on the solubility of manganese than they are on the solubility of iron. Hence, amounts of manganese from a few-hundredths ppm to 1.0 ppm may often be retained in solution at equilibrium, either in ground water or in surface water. However, at a pH above 8, oxidation by air may lower the concentration of dissolved manganese to less than 0.01 ppm.

Rates of manganese oxidation are increased by raising the pH and are decreased by the presence of SO_4^{-2} or HCO_3^- . The oxidation and the precipitation reactions are complex and may yield mixed products. Experimental studies indicated that the reactions are first order with respect to manganese, but that the rates are increased by autocatalytic effects of the oxides produced.

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