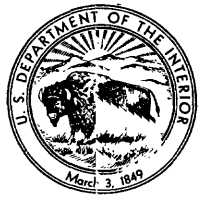
Reduction and Complexing of Manganese by Gallic Acids

By JOHN D. HEM

CHEMISTRY OF MANGANESE IN NATURAL WATER

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1667-D

Chemical reactions with organic acids which influence the behavior of manganese in natural water



UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1965

UNITED STATES DEPARTMENT OF THE INTERIOR

STEWART L. UDALL, *Secretary*

GEOLOGICAL SURVEY

Thomas B. Nolan, *Director*

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 - Price 20 cents (paper cover)

CONTENTS

	Page
Abstract	D1
Introduction	1
Previous work	1
Behavior of manganese in lakes	2
Organic materials in natural water	4
Properties of tannic acid	5
Digallic acid complex with manganese	6
Determination of stability constant	8
Properties of gallic acid	10
Complexes of Mn^{+2} with other organic ligands	11
Complexes with higher oxidation states of manganese	12
Solution of manganese dioxide by digallic acid	13
Calculation of amount of manganese complexed	20
Solvent-extraction experiments	22
Stability of complex toward oxidation	22
Solution of manganese dioxide by gallic acid	23
Effects of gallic acid compared with those of digallic acid	25
Importance of reducing and complexing in natural systems	25
Literature cited	27

ILLUSTRATION

	Page
FIGURE 1. Solution of manganese by tannic acid at (*A*) pH 5.5 and (*B*) pH 8.5	D15

TABLES

	Page
TABLE 1. Computation of stability constant for manganese digallate complex	D9
2. Manganese concentration and pH of solutions in contact with manganese dioxide. Tannic acid absent	14
3–6. Manganese concentration, pH, and Eh of—	
3. 10-ppm tannic acid solution in contact with manganese dioxide	16
4. 100-ppm tannic acid solution in contact with manganese dioxide	16
5. 1,000-ppm tannic acid solution in contact with manganese dioxide	17
6. Solutions of gallic acid in contact with manganese dioxide	24

CHEMISTRY OF MANGANESE IN NATURAL WATER

REDUCTION AND COMPLEXING OF MANGANESE BY GALLIC ACIDS

By JOHN D. HEM

ABSTRACT

Tannic (digallic) and gallic acids form 1:1 complexes with Mn^{+2} in dilute solution. The stability constant of the digallic complex was determined to be $10^{3.9}$ by spectrophotometric studies. Water solutions of tannic and gallic acid can bring 100 parts per million or more of manganese into solution from solid manganese dioxide reagent. The reducing and complexing reactions are most rapid at pH's below 5. The manganese brought into solution was oxidized very slowly at pH's as high as 9.8.

INTRODUCTION

The biochemical factors that are involved in the chemical behavior of manganese in natural environments have been touched upon in the earlier papers in this series. A further study of some chemical reactions that may influence manganese solution and deposition is described here. The study concerns the behavior of oxidized and reduced forms of manganese in the presence of the organic compounds tannic acid and gallic acid. The rates of reduction of tetravalent manganese by the organic acids, and the form and stability of the soluble manganese compounds formed in the reduction process, were investigated. The results provide some indications as to the principles which govern the circulation of manganese in natural environments at or near the land surface, where organic material is plentiful.

PREVIOUS WORK

Preliminary studies of the behavior of divalent manganese in dilute solutions of tannic acid were described by the writer in an earlier report (Hem, 1963, p. A51–A52), but no definite conclusions were drawn. A green color was observed in solutions containing tannic acid and divalent manganese, and a similar color was noted when the

pH of the tannic acid solutions was increased in the absence of manganese. Tannic acid noticeably retarded the rate of oxidation of divalent manganese when the alkaline solutions were exposed to the air. In some environments, such as bogs, that are rich in organic matter, the effects of organic solutes are unquestionably important. In this paper reduction and complexing effects have been studied in detail so that their importance could be intelligently evaluated. Some preliminary results of experiments with tannic-acid reduction of manganese dioxide have been reported by Rawson (1963).

BEHAVIOR OF MANGANESE IN LAKES

One of the more common water-quality problems encountered in the water-supply industry is the appearance of manganese in solution in the water withdrawn from a supply reservoir. The literature contains many references to this type of problem, with descriptions of conditions found and methods used for coping with the problem. The causes, however, have not always been clearly understood or satisfactorily explained.

Vegetation requires manganese in its life processes, and some of the aquatic species of plants seem to accumulate the element (Oborn, 1964). Hutchinson (1957, p. 805) states that the manganese content of lake water is directly related to the productivity of the lake. Lakes and reservoirs support a considerable volume of aquatic vegetation, ranging in size from diatoms to large water weeds rooted in the lake bottom, and during the growing season as much as 10 tons of dry cellulose and related material could be produced per acre of water surface (Lieth, 1963). This high production rate is probably more typical of sewage-oxidation ponds or peat-bog or swamp environments than of a clear lake, but any water impoundment can be expected to produce a considerable mass of organic matter each year. In his studies of productivity in several lakes in Denmark, Nygaard (1953) found a production rate of organic matter of 0.62 g per day per square meter in relatively clear water 28 meters deep. This rate is equivalent to more than a third of a ton per acre in a growing season of 150 days and is probably lower than the usual rate for a storage reservoir. In large part, the organic matter produced in each growing season decays, and a residue of low-solubility material settles to the lake bottom.

Organic matter of aquatic vegetation contains from a few hundredths to a few tenths of a percent of manganese (Oborn, 1964). The amount of manganese present depends partly on its availability. Bottom-rooted plants can extract manganese from the soil below the water surface, but free-floating forms can obtain it only from the water in which they grow.

The quantitative importance of biological productivity as a mechanism for trapping manganese in a lake can be estimated in several ways. The amount of manganese in solution brought into a reservoir during the growing season probably is normally almost all removed biologically. The median manganese concentration of North American rivers of major size is reported by Durum and Haffty (1963) to be 20 micrograms per liter. Thus, in 1 acre-foot of water, one might expect to find about 25 g of manganese. The median concentration of 20 micrograms per liter is equivalent to 0.02 ppm (parts per million) and is a higher concentration than might be expected from the rather sparse data for manganese content in the analytical records published by the U.S. Geological Survey in annual reports on quality of surface water of the United States. In keeping with longstanding custom, the dissolved constituents in river water are ordinarily determined on filtered or clarified samples. Durum and Haffty used samples which had been filtered and acidified, but the filtration did not remove all the particulate matter. Hence, their results may include some of the particulate manganese that was present. Hutchinson (1957) indicates that particulate manganese may be utilized by plants and in any event is likely to be precipitated in a standing water body such as a lake or reservoir.

A production rate of one-quarter ton of dry vegetation per acre of lake surface per year, of material containing 0.10 percent manganese, would represent a rather modest productivity and would require 250 g of manganese per acre of lake surface. The amount of manganese available from lake water having 20 micrograms of manganese per liter, or 25 g of dissolved manganese per acre-foot, is enough to supply the biochemical demand for the whole year if the photosynthetic process is active to a depth of 10 feet. An annual inflow of water sufficient to renew the manganese supply would be required to maintain the process. Bottom-rooted aquatic species growing in shallow water would extract some of their manganese from the soil of the lake bottom. When the growing season ends, the crop of vegetation dies back and the debris settles toward the bottom of the lake. This debris carries with it at least a part of the manganese originally incorporated in the vegetation and forms an organic-rich precipitate.

Biological processes, therefore, tend to remove manganese from water and transfer it to a lake-bottom precipitate in significant amounts. The normal circulation of aerated water through the lake maintains oxidizing conditions and depresses manganese solubility. During periods of thermal stratification, however, the deeper water may be depleted in oxygen through biochemical processes to a degree that induces reduction and re-solution of manganese in water near the bottom muds that contain the manganese placed there earlier

through the decay of vegetation. The volume of water, so affected, will generally be small compared with the volume from which this manganese was originally extracted. Thus, the effect of a 10-fold or 100-fold concentration could readily be achieved, leading to a manganese concentration in the bottom water of 0.2 ppm or 2.0 ppm instead of 20 micrograms per liter. Concentrations higher than a few tenths parts per million lead to problems if introduced into water distribution systems. Intakes may obtain such water if they are oriented in such a way as to intercept bottom water, or if the bottom water migrates to other levels.

Although the biochemical processes of manganese removal and occasional re-solution can probably account for the usual occurrences of manganese in water of storage reservoirs, the actual processes in the bottom sediments may involve some additional factors related to organic complexing and reduction. In a few areas, such as the piedmont region of Georgia studied by Ingols and Wilroy (1963), the manganese content of the material making up the original bottom of the reservoir may be high enough to be a significant source of manganese for solution.

ORGANIC MATERIALS IN NATURAL WATER

The nature of naturally occurring organic solutes in colored river and lake water has never been completely established, even though such materials have been extensively studied. Lamar and Goerlitz (1963), however, were able to identify 12 carboxylic acids in unpolluted surface water from streams in the States of California and Washington. Substances identified included acetic, propionic, butyric, valeric, caproic, lactic, malonic, maleic, succinic, adipic, fumaric, and oxalic acids. The concentrations observed were from 4 to 592 parts per billion. Other carboxylic acids of higher molecular weight were also isolated but could not be specifically identified by gas chromatography because they were relatively stable and nonvolatile. Such acids have commonly been referred to in the literature as "humic" or "fulvic," or are given other names, which imply a definite chemical formula or structural pattern. Actually these names have been used with various connotations by many different writers to refer to complex mixtures of high molecular weight organic acids and polymers which impart a brown or yellow color to water and can be extracted by certain empirical procedures. The color and probably the structure of these materials are partly a function of pH and it has not been agreed whether they occur in true solution or as a colloidal suspension. The molecules of these substances may actually approach colloidal size.

Shapiro (1964) conducted extensive studies of organic coloring matter which he extracted from lake water which he refers to as

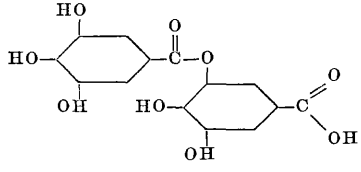
"yellow organic acids" and has determined to be a mixture of aliphatic polyhydroxy carboxylic acids.

Black and Christman (1963a, b) suggested that the organic material responsible for color observed in many natural river waters consists of hydroxycarboxylic acids which have some degree of unsaturation and aromaticity. Their material also contained between 1 and 2 percent nitrogen. Lamar and Goerlitz (1963) reported that the infrared spectrum of colored material obtained from one of their waters resembled that of metadigallic acid, and the studies of Black and Christman (1963b) also indicate that such a compound can be expected in colored natural water. Therefore, it is possible to obtain some useful indications of the behavior of manganese in natural waters by studying the reactions between manganese and digallic (tannic) acid. Tannic acid is readily available in relatively pure form. Another series of experiments was performed with gallic acid, $C_6H_2(OH)_3COOH$, in the expectation that the simpler compound would be more stable and easier to work with.

The results of experiments with well-defined chemical compounds can be expressed in relatively exact terms, with respect to the nature of reactions and products and to the stability of complex ions which are produced. However, results of experiments with the natural organic materials extracted from water are usually less exact.

PROPERTIES OF TANNIC ACID

Tannic acid (digallic acid) has the chemical formula $(HO)_3C_6COO\ C_6H_2(OH)_2COOH$, and can be represented structurally as



It is formed by hydrolysis from the more complex substances called tannins. Tannins are commonly present in vegetation, and therefore natural water, which usually has some contact with plant debris, commonly contains tannic acid or chemically similar material in solution.

The reagent-grade tannic acid used in this work was a pale yellow-brown powder, which dissolved readily in water. Solutions containing 1 mg of reagent per ml of water were pale yellow, and at this concentration had a pH near 4.0.

In earlier work (Hem, 1960, p. 78) the writer estimated the first dissociation constant for tannic acid to be about 10^{-6}. The curves obtained in potentiometric titrations of the tannic acid with strong base gave no well-defined inflection points but seemed to suggest that

the carboxyl hydrogen is mostly titrated before the phenolic hydrogens are detached from the molecule. The amount of base consumed, however, suggests that some influence from the phenolic hydrogens is probably present at pH 8 and that this influence increases as pH increases.

Redox titrations of tannic acid at various pH's using potassium permanganate and platinum and saturated calomel electrodes were performed to evaluate the reducing ability of the reagent. In these titrations the manganese was at first reduced from Mn^{+7} to Mn^{+2}, but ultimately a black flocculent precipitate, or a dark-brown colloidal suspension, containing Mn^{+4}, was produced. These experiments indicate that solutions of digallic acid are definitely capable of reducing manganese to the Mn^{+2} state, and that their ability for reduction is increased by lowering the pH.

The chemical mechanisms involved in the reduction of permanganate by digallic acid were not definitely ascertained. The color of the solution suggests that the organic compound undergoes considerable alteration in the process. For the present study, the processes of oxidation and reduction which are of interest are those involving Mn^{+2} and Mn^{+4}, and therefore no detailed investigations of the effects of permanganate on digallic acid seemed necessary.

The amount of permanganate which reacted with 10 mg (3.1×10^{-5} moles) of digallic acid without precipitating manganese oxide at pH 7.0 was about 6×10^{-5} moles. The conversion of one MnO_4^- ion to Mn^{+2} involves the gain of five electrons. Hence, the reduction equivalency of digallic acid in the conditions of this particular experiment was about 10 times its molality. One mole of tannic acid, therefore, should be capable of reducing 5 moles of Mn^{+4} to Mn^{+2}.

If, in being oxidized, the digallic acid molecule loses all 5 of its phenolic groups, and they are replaced with hydrogen, the net effect on the nominal charges on the carbon atoms in the 2 benzene rings is equivalent to the loss of 10 electrons. This mechanism would, therefore, be in accord with the results of the permanganate titration.

DIGALLIC ACID COMPLEX WITH MANGANESE

In earlier work (Hem, 1960), digallic acid appeared to form complexes with ferrous iron, and the possibility of similar complex formation with manganous ions was investigated. Aliquots were prepared containing 5.0 mg and 10.0 mg of digallic acid and small amounts of Mn^{+2} ranging from 0.02 to 1.0 mg. These aliquots were adjusted to pH 7.0 with 0.016-molar sodium hydroxide, diluted to 25 ml, and the intensity of the green color which formed was measured with a spectrophotometer after the aliquots stood for 2 hours to

permit complete color development. Maximum absorbance occurred at 400 mμ. A direct linear response was obtained for the lower concentrations of manganese (up to about 0.15 mg of manganese in 25 ml of water). This response indicates a complex, whose behavior was in accord with Beers' law, in dilute solution. As the concentration of manganese was increased, however, a maximum color intensity was reached beyond which further increases in manganese content brought about no change.

The composition of the complex was determined from the spectrophotometric data using the procedure of Yoe and Jones (1944). In this procedure the absorbance is determined for various mole ratios of ligand to manganese. Straight parts of the resulting curve are extrapolated to an intersection which indicates the mole ratio of the predominant complex. A 1:1 mole ratio of manganese and digallic acid was indicated, at least for the concentrations of the reactants used here (about 10^{-4} to 10^{-6} molar) and at a pH near or slightly above neutrality.

The intensity of the green color was a function not only of manganese and digallic acid activities, but also of pH; the rate at which the color developed was also influenced by pH. The color was more intense at pH 8 than at pH 7 and developed more rapidly at the higher pH. After about 2 hours, at pH 7 and pH 8, the color stabilized and did not change significantly during the next 12–16 hours. Some greenish color was observed in solutions of digallic acid without manganese, when made alkaline with sodium hydroxide. The hue in these solutions, however, was somewhat different from that developed when manganese was present, and the intensity was generally much less when manganese was absent.

The color in these solutions is apparently associated with changes of the molecular configuration of the digallic acid. Such changes are probably brought about to some extent by neutralization with strong base which may displace some of the phenolic hydrogens. The fact that the color development is stronger in the presence of manganese and at higher pH's suggests that the two positive charges of the manganese ion are probably attracted both to the carboxyl and phenolic sites on the digallic acid molecule when the hydrogens in these positions are displaced.

If the digallate ligand is attached to the Mn^{+2} cation, both at the carboxyl and phenolic positions, the 1:1 complex would be uncharged. Perhaps this form would become more abundant as the pH is increased. However, in the absence of positive evidence as to the charge of the complex species, a linkage at only one position has been assumed.

DETERMINATION OF STABILITY CONSTANT

The stability constant of the manganous-digallate complex was determined from the spectrophotometric data using the following lines of reasoning:

The digallate ligand, represented by the symbol T^-, is considered to be the form of tannic acid present in the solutions on removal of the carboxyl hydrogen, and possibly one or more of the phenolic hydrogens, as a result of raising the pH. Solutions used in the experiments were about 10^{-4} molar. In media having so low an ionic strength (near 10^{-4}), the ion activity coefficients, represented by the symbol γ, are near unity. The quantities in brackets are ion activities, the C terms are measured concentrations.

The association equilibrium

$$Mn^{+2}+T^-=MnT^+$$

when written in mass-law form is

$$\frac{[MnT^+]}{[Mn^{+2}][T^-]}=K_1, \tag{1}$$

and the constant K_1 is the stability constant for the 1:1 complex. The total amount of manganese present is either in the complexed or uncomplexed form

$$\sum C_{Mn}=\frac{[Mn^{+2}]}{\gamma_{Mn^{+2}}}+\frac{[MnT^+]}{\gamma_{MnT^+}}. \tag{2}$$

The dissociation of digallic acid can be assumed to be very nearly complete at pH 8.0, because the first dissociation constant is near 10^{-6}. Accordingly, the undissociated form can be ignored, and one may equate the total concentration of the ligand present to two forms

$$\sum C_T=\frac{[MnT^+]}{\gamma_{MnT^+}}+\frac{[T^-]}{\gamma_{T^-}}. \tag{3}$$

The optical density observed in the solutions was used as a measure of the amount of manganese complexed. The spectrophotometer readings were adjusted for the effects of absorbance by digallic acid by means of blanks containing no manganese, and the measurements were all made with the same length of light path. Under these conditions, for any given manganese concentration, a maximum optical density can be obtained by increasing the proportion of digallic acid to manganese in the solution. This maximum value represents the point at which essentially all the manganese has been complexed. For solutions containing the same amount of manganese, but not enough

digallic acid to develop the maximum optical density, a lower optical-density value will be observed, and the ratio of total manganese to complexed manganese will follow the relation

$$\frac{\sum C_{Mn}}{C_{MnT}} = \frac{\text{maximum optical density}}{\text{observed optical density}}. \quad (4)$$

Experimental data for seven different laboratory samples are given in table 1. They may be used to provide solutions for equations 1 to 4. In these solutions manganese concentrations ranged from 7.3×10^{-6} to 7.3×10^{-5} molar, and digallic acid concentrations ranged from 1.2×10^{-4} to 6.2×10^{-4} molar. Maximum ionic strength in these solutions was 4.8×10^{-4}. At this ionic strength, all activity coefficients are close to 1.0. Values for γ_{MnT} and for γ_T cannot be readily computed from the Debye-Hückel equation; therefore, they were assumed to be unity. This assumption introduces an error of less than 5 percent into the values for K_1. Values for $\gamma_{Mn^{+2}}$ were obtained from the Debye-Hückel equation—using the concentrations of Mn^{+2}, Cl^-, Na^+, and T^-—without complexing to calculate the ionic strength. The effect of complexing on the ionic strength could have been corrected for by further computation but this was not done because the spectrophotometric data could not be reproduced very closely. Values for K_1 range from 1.4×10^4 to 5.5×10^3. The mean of the seven values is 8.2×10^3 or $10^{3.9}$.

The uncertainties in the experimental data limit the accuracy of the constant. The pH had a considerable effect on the depth and stability of the color developed, and most of the range observed in K_1 values in table 1 can probably be attributed to this factor. The true value of K_1 could be higher or lower than the value calculated here by a factor of 2.

TABLE 1.—*Computation of stability constant for manganese digallate complex*

Sample	Total manganese ΣC_{Mn} (moles per liter)	Total digallic acid ΣC_T (moles per liter)	Absorbence		K_1
			Maximum	Observed	
1	3.6×10^{-5}	2.5×10^{-4}	0.44	0.250	6.4×10^3
2	3.6×10^{-5}	6.2×10^{-4}	.44	.390	1.4×10^4
3	7.3×10^{-5}	2.5×10^{-4}	.88	.48	6.2×10^3
4	7.3×10^{-6}	1.2×10^{-4}	.46	.240	9.6×10^3
5	3.6×10^{-5}	1.2×10^{-4}	.79	.305	6.0×10^3
6	7.3×10^{-5}	1.2×10^{-4}	1.20	.53	9.6×10^3
7	1.5×10^{-5}	1.2×10^{-4}	.55	.212	5.5×10^3
Mean					8.2×10^3

The behavior of ferrous iron in digallic acid solution at pH 5.0 was considered earlier by the writer (Hem, 1960). For an assumed 1:1 complex the stability constant was estimated to be about 10^{13}, based

on the interference of digallic acid with the formation of the pink complex of dipyridyl and ferrous iron.

Ferrous complexes with organic ligands are considerably stronger, as a rule, than the corresponding manganese complexes. However, the difference between the stability constants for manganese and ferrous complexes with digallic acid seems excessive. The composition of the ferrous complex was not determined, and it may be that the simple FeT^{+} structure that was assumed is incorrect.

The chemical behavior of the digallic acid reagent used in this series of experiments was not exemplary for exacting quantitative studies. The solutions of the acid were not stable in contact with air and slowly darkened in color on standing. Changes in the molecular configuration and complexing behavior, which might have resulted, were avoided by using freshly prepared solutions. Complexing and neutralization reactions were relatively slow, and the green complex tended to change color after a day or so, probably because of oxidation. The amount of color development and the rate of complexing were strongly influenced by pH. Close agreement of results in successive sets of samples therefore was not always attained.

The strength of the digallic complex suggests that in solutions containing about 10 ppm of digallic acid and a few tenths of a part per million or less of manganese, the manganese would be about 50 percent complexed. Solutions of this kind may occur in rivers and lakes, although the nature of the organic matter in such water is probably not the same as the material studied. Natural coloring matter can be expected to have significant effects both as a reducing agent and as a complexing agent.

PROPERTIES OF GALLIC ACID

Experiments using gallic acid were compared with those using tannic acid. The reagent grade gallic acid used in these experiments was a white powder, having the chemical formula $(HO)_3C_6H_2COOH \cdot H_2O$. The solutions of this material were colorless at first but tended to darken with age. Both gallic and digallic acids seemed to serve as nutrients for fungi which grew luxuriantly in some of the solutions left in the open air. Biological growths, however, were prevented from forming in the solutions used in the actual experiments.

The first dissociation constant for gallic acid is reported to be 4×10^{-5} (Lange, 1956). The acidic properties are therefore stronger than those of digallic acid. Potentiometric titrations, using glass and saturated calomel electrodes, indicated a single well-defined inflection at pH 6.2. The phenolic hydrogen on the gallic acid molecule appears not to be active as a source of protons until the pH has increased

considerably beyond 6.2, but phenolic hydrogens probably become available at about pH 8.

Gallic acid is an effective reducing agent and, like digallic acid, reacts with permanganate ions to yield Mn^{+2}.

In the titration of gallic acid solutions with sodium hydroxide, a green color was observed which increased in intensity when the pH increased. This color probably resulted from the disruption or rearrangement of the gallic acid molecules. A very similar color was observed when gallic acid and manganese solutions were mixed and the pH adjusted. When manganese was present, however, the color appeared more rapidly and at a lower pH. The color developed in the presence of manganese was a more yellowish shade of green.

The nature of the complex formed between gallic acid and divalent manganese has been studied by Kachhawaha and Bhattacharya (1962). These investigators used higher concentrations of reactants and worked at a lower pH than in the work described here, but they did report a green color in some of their solutions. They reported a 1:1 complex whose stability constant is $10^{2.16}$. This compares with the value $10^{3.9}$ for the 1:1 complex of divalent manganese and digallic acid determined in the present experiments.

Observations in the current study indicate that the gallic acid complex is weaker than the digallic complex, although perhaps not as much weaker as the difference between the two constants would indicate. A preliminary series of experiments in which the gallate complex was developed at pH 7 in the presence of different amounts of manganese and gallic acid gave results which indicated the 1:1 association constant was between 10^2 and 10^3. The value of Kachhawaha and Bhattacharya is in the lower part of this range. Hence, refined experimental work to determine the constant more closely was not undertaken.

COMPLEXES OF Mn^{+2} WITH OTHER ORGANIC LIGANDS

The compilation of Bjerrum, Schwarzenbach, and Sillen (1957) includes stability constants for a 1:1 complex of divalent manganese with several other organic acids which may occur in natural water. The acids and constants for the type reaction (where M is the metal ion and L is the organic ligand)

$$M+L=ML$$

are as follows: Oxalic acid, $K=10^{2.55}$–$10^{3.96}$; malonic acid, $K=10^{3.29}$. It would appear that complexes of divalent manganese with the organic ligands likely to occur in natural waters have similar stabilities.

Concentrations of a few tens of parts per million of organic acids would be necessary in order to complex half of the dissolved manganese. Until more information on the concentrations of manganese in natural water is available, the importance of complex formers such as these in influencing the behavior of other solutes cannot be evaluated.

COMPLEXES WITH HIGHER OXIDATION STATES OF MANGANESE

The oxidation state of manganese, which normally is to be expected in natural water, is Mn^{+2}. Thermodynamic data in the literature show that oxidation of the divalent form will normally produce Mn^{+4} (Hem, 1963), and most aqueous species of trivalent manganese which might be formed as intermediate products are unstable. Some organic complexes of trivalent manganese are known, however. For example, complexes of oxalate ions with trivalent manganese are formed at an intermediate stage in the oxidation of oxalate by permanganate in acid solution. The mechanism of this oxidation reaction has been rather extensively studied and several values for stability constants of the oxalate complexes with trivalent manganese are quoted in Bjerrum, Schwarzenbach, and Sillen (1957). Although the complexes are strong in the sense that most trivalent manganese in solution is tied up on the complexes, they are very susceptible to oxidation. The literature is in general agreement that trivalent manganese is unstable in aqueous solution and can be expected to revert either to divalent or to quadrivalent forms. Strictly speaking, an equilibrium model therefore need not consider trivalent species. However, some consideration must always be given to metastability, and the rate of oxidation of divalent manganese was considerably retarded by the organic acids studied in the work here described. Some writers have expressed the view that manganese in natural water may often occur in the trivalent state, presumably either as a metastable complex or perhaps as a colloidal or molecularly dispersed hydroxide.

The solid species of manganese oxide to be expected in natural environments were considered in an earlier paper (Hem, 1963). The standard free-energy values used for that report indicated that the hydroxide $Mn(OH)_3$ was unstable with respect to dehydrated species, but some indication of hydrated partly oxidized forms was found in laboratory studies of oxidation of Mn^{+2} solutions in air. It is possible, however, to assign a mixed-oxide composition to compounds such as Mn_2O_3, which thus becomes $MnO \cdot MnO_2$ or to Mn_3O_4 which becomes $2MnO \cdot MnO_2$.

Studies of some of the manganese oxide precipitates obtained in the laboratory were made by X-ray diffraction methods, and patterns corresponding to hydrohausmannite, a hydrated form of Mn_3O_4, de-

scribed by Frondel (1953) were sometimes obtained. (More recently, Feitknecht, Brunner, and Oswald (1962) have reported that material prepared and termed hydrohausmannite in earlier experiments was actually a mixture of hausmannite and beta MnO(OH).) The bulk of the material was too poorly crystallized to give any X-ray pattern. In some of the digallic and gallic acid solutions containing dissolved manganese, a flocculent black precipitate formed after the solutions had stood for several months in contact with air. This material gave no distinguishable X-ray pattern. Some of the solutions took on a brown color, perhaps owing to some form of complex of partly oxidized manganese, but possibly also explainable as an organic oxidation product, or a colloidal suspension of manganese dioxide. The brown color could be extracted from these solutions with amyl alcohol, which suggests the material was organic and the result of oxidation of the organic acid.

In a series of solvent-extraction experiments, manganese was left behind in the water fraction. The water solutions were clear and colorless, and no precipitates of oxide formed. These facts suggest that the complexed manganese was originally in the Mn^{+2} form. Some additional evidence against higher oxidation states in the complexed manganese is the approximate agreement between the calculations of amounts complexed from the Eh-pH data and the results obtained using the stability constant where the Mn^{+2} state was assumed at the beginning. These calculations and the solvent extraction studies are discussed later in this paper.

This evidence is not complete proof that organic complexes of trivalent manganese do not occur in natural water. Under the conditions of these experiments, however, manganese evidently did not occur in that state.

SOLUTION OF MANGANESE DIOXIDE BY DIGALLIC ACID

The effectiveness of digallic acid as a reducing agent for manganese dioxide was studied in a series of experiments. Solutions containing 10, 100, and 1,000 milligrams per liter of tannic acid reagent were prepared. Six aliquots of each solution were adjusted in pH by using potassium hydroxide or hydrochloric acid, as required, to give a series of 18 solutions having pH's of 4.5, 5.5, 6.5, 7.5, 8.5, and 9.5. About 500 ml of each solution was placed in a polyethylene bottle, and 1.0 g reagent-grade manganese dioxide powder was introduced. In addition to the 18 bottles containing tannic acid solutions, a group of six bottles was prepared containing distilled water, to which was added first enough acid or base to give the desired pH and then manganese dioxide. Air was not excluded from these solutions, owing to the permeability of polyethylene for gases.

769-002—65——3

The solutions were allowed to stand at a temperature of 25°C and, from time to time, portions were removed for determination of pH and of redox potential. At the same time, an aliquot was filtered through a plastic membrane filter having pore diameters of 0.45μ, and analyzed for dissolved manganese using the standard periodate procedure. The bottles were shaken about once a day to keep the contents mixed. The solutions remaining after 2 months were filtered into new bottles, and some further experiments were performed on these portions.

The results of the determinations are given in tables 2–5. Some indication of the nature of the reactions that took place in these solutions can be gained by examination of these data. General trends can be summarized as follows:

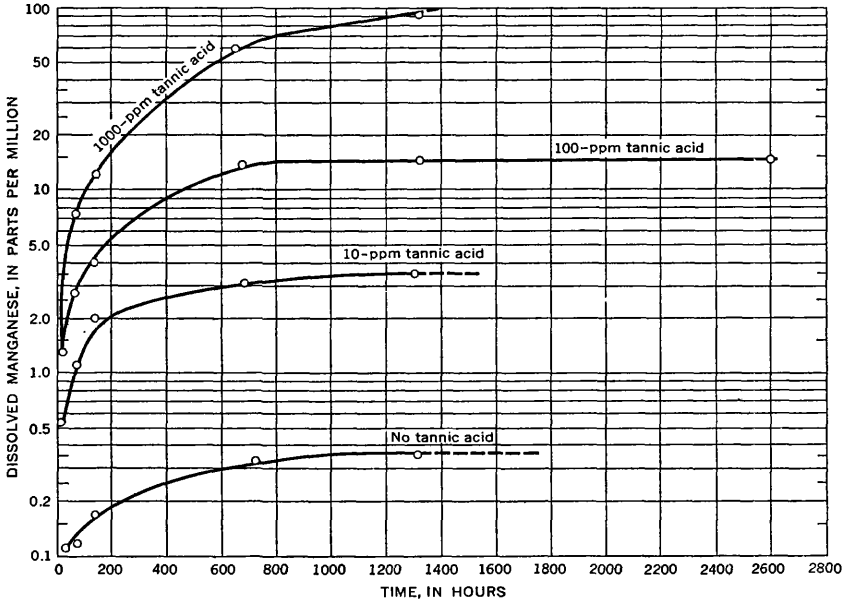
1. Manganese in solution at first increased with time, but tended eventually to reach a stable plateau.
2. More manganese went into solution when the amount of tannic acid was increased.
3. Amounts of manganese dissolved were greatest in solutions that were started at low pH.
4. The solutions containing tannic acid at an initial pH above 7 decreased in pH on standing. The more acid solutions increased in pH. Final pH values were generally between 6.5 and 7.0.
5. The Eh of all the solutions tended generally to increase with time, at first rapidly and then more slowly.
6. Very little manganese was dissolved in the absence of tannic acid.
7. Solutions containing tannic acid and manganese were colored green in the early part of the experiment but later a brown color developed which tended to obscure the original green. The solutions still absorbed light strongly at the wave length used in studies of the complex.

TABLE 2.—*Manganese concentration and pH of solutions in contact with manganese dioxide*

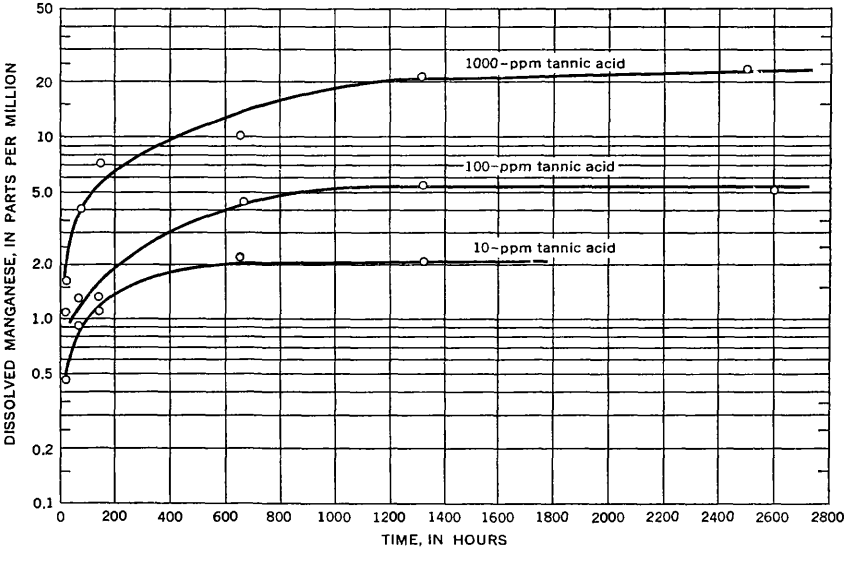
[Tannic acid absent]

Time (hours)	Manganese concentration and pH of solutions in contact with manganese dioxide for the initial pH indicated											
	4.5		5.5		6.5		7.5		8.5		9.5	
	Mn	pH	Mn	pH	Mn	pH	Mn	pH	Mn	pH	Mn	pH
0	0.0	4.50	0.00	5.50	0.00	6.50	0.00	7.50	0.00	8.50	0.00	9.50
3	------	4.97	------	5.85	------	6.48	------	6.76	------	6.90	------	9.08
24	.11	4.85	.11	5.65	.07	6.07	.07	6.59	.03	6.77	.07	8.80
72	.12	4.98	.12	5.72	.07	6.27	.07	6.58	.04	6.69	.04	8.01
144	.24	4.98	.17	5.71	.06	6.20	.06	6.38	.05	6.40	.01	7.00
720	.51	5.20	.33	5.58	.13	5.81	.06	6.20	.06	6.21	.03	6.41
1,320	.61	5.60	.36	5.88	.36	5.43	.08	6.01	.08	6.03	.04	6.32

The rate at which manganese was dissolved is indicated graphically in figure 1 for solutions initially brought to pH 5.5 and pH 8.5. The



A. Initial pH 5.5.



B. Initial pH 8.5.

FIGURE 1.—Solution of manganese from manganese dioxide by different concentrations of tannic acid.

TABLE 3.—*Manganese concentration, pH, and Eh of 10-ppm tannic acid solution in contact with manganese dioxide*

Time (hours)	Manganese concentration, pH, and Eh of 10-ppm tannic acid solution in contact with manganese dioxide for the initial pH indicated																					
	4.5				5.5				6.5				7.5				8.5				9.5			
			Eh (volts)				Eh (volts)				Eh (volts)				Eh (volts)				Eh (volts)			
	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated
0	0.0	4.50	------	------	0.0	5.50	------	------	0.0	6.50	------	------	0.0	7.50	------	------	0.0	8.50	------	------	0.0	9.50	------	------
3	------	5.28	0.58	------	------	6.17	0.53	------	------	6.60	0.49	------	------	7.05	0.47	------	------	7.34	0.46	------	------	8.66	0.39	------
21	.64	5.55	.55	0.72	.53	6.10	.52	0.64	.51	6.50	.50	0.60	.47	6.69	.48	0.58	.46	6.93	.50	0.56	.18	8.50	.43	0.37
70	1.1	6.06	.56	.64	1.1	6.39	.55	.60	.88	6.66	.53	.58	.88	6.75	.53	.56	.94	6.70	.55	.52	.24	7.49	.50	.49
142	1.8	6.15	.56	.63	2.0	6.27	.55	.61	1.1	6.42	.53	.60	1.2	6.60	.53	.57	1.1	6.60	.56	.57	.75	6.88	.55	.55
646	3.0	6.14	.61	.62	3.1	6.32	.59	.60	2.0	6.32	.59	.61	1.8	6.55	.59	.58	2.2	6.61	.58	.56	.86	6.80	.58	.56
1,320	3.6	6.19	.60	.62	3.5	6.60	.59	.57	2.4	6.60	.59	.57	1.8	6.59	.58	.57	2.0	6.60	.58	.57	.79	6.70	.56	.57

TABLE 4.—*Manganese concentration, pH, and Eh of 100-ppm tannic acid solution in contact with manganese dioxide*

Time (hours)	Manganese concentration, pH, and Eh of 100-ppm tannic acid solution in contact with manganese dioxide for the initial pH indicated																					
	4.5				5.5				6.5				7.5				8.5				9.5			
			Eh (volts)				Eh (volts)				Eh (volts)				Eh (volts)				Eh (volts)			
	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated
0	0.0	4.50	------	------	0.0	5.50	------	------	0.0	6.50	------	------	0.0	7.50	------	------	0.0	8.50	------	------	0.0	9.50	------	------
3	------	5.58	0.54	------	------	6.02	0.52	------	------	6.52	0.49	------	------	7.00	0.49	------	------	7.43	0.48	------	------	8.59	0.41	------
21	1.7	5.83	.52	0.67	1.3	5.98	.53	0.66	1.2	6.30	.51	0.61	1.2	6.42	.52	0.60	1.1	6.79	.51	0.55	.74	7.29	.48	0.50

70	3.2	5.99	.47	.64	2.8	5.98	.48	.64	2.3	6.16	.49	.62	1.6	6.35	.49	.62	1.3	6.57	.49	.58	.88	6.76	.48	.57
142	4.9	5.90	.50	.66	4.2	5.98	.50	.63	3.2	6.00	.50	.64	2.3	6.18	.50	.62	1.3	6.39	.50	.60	1.3	6.75	.50	.56
670	20	6.45	.58	.56	14	6.58	.57	.55	13	6.37	.57	.57	8.7	6.22	.57	.60	4.4	6.40	.57	.59	4.4	6.50	.58	.58
1,320	21	6.87	.56	.50	14	6.78	.57	.52	13	6.91	.56	.50	[4]10	6.91	.58	.51	[5]5.2	6.92	.58	.52	[6]5.2	7.00	.57	.50
2,600	[1]19	6.90	.54	.50	[2]14	6.89	.54	.51	[3]13	6.78	.54	.52	9.3	6.71	.55	.55	5.0	6.79	.54	.54	4.0	6.94	.53	.52

Percentages of manganese as complex, calculated from stability constant and from Eh and pH, respectively, are as follows for the footnoted concentrations:
[1] 46 and 79. [3] 53 and 98. [5] 67 and 99.
[2] 59 and 88. [4] 61 and 99. [6] 66 and 99.

TABLE 5.—*Manganese concentration, pH, and Eh of 1,000-ppm tannic acid solution in contact with manganese dioxide*

Time (hours)	Manganese concentration, pH, and Eh of 1,000-ppm tannic acid solution in contact with manganese dioxide for the initial pH indicated																							
	4.5				5.5				6.5				7.5				8.5				9.5			
			Eh (volts)				Eh (volts)				Eh (volts)				Eh (volts)				Eh (volts)			
	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated
0	0	4.50	------	------	0	5.50	------	------	0	6.50	------	------	0	7.50	------	------	0	8.50	------	------	0	9.50	------	------
3	------	4.88	0.55	------	------	5.88	0.48	------	------	6.49	0.48	------	------	7.12	0.48	------	------	8.29	0.43	------	------	9.16	0.36	------
24	3.6	5.12	.55	0.74	1.3	5.70	.51	0.69	1.2	5.96	.51	0.65	1.8	6.58	.49	0.57	1.6	7.67	.45	0.44	.66	8.40	.41	0.37
72	8.4	5.50	.51	.68	7.3	5.5	.53	.70	2.2	5.66	.54	.68	2.2	6.09	.53	.63	4.0	6.88	.49	.53	.80	7.41	.46	.48
144	15	5.57	.51	.67	12	5.57	.53	.67	7.1	5.75	.53	.66	2.4	6.08	.54	.63	7.2	6.49	.53	.57	1.0	6.69	.51	.57
646	71	5.58	.47	.65	59	5.65	.49	.65	50	5.99	.51	.60	32	6.02	.51	.61	9.8	6.28	.51	.59	3.2	6.47	.51	.60
1,320	112	6.35	.51	.54	90	6.25	.52	.57	80	6.40	.54	.55	54	6.40	.55	.55	21	6.62	.54	.55	15	6.75	.53	.52
2,500	------	6.68	.54	------	------	6.59	.54	------	89	6.68	.55	.52	59	6.67	.56	.53	23	6.90	.56	.53	22	6.78	.55	.51

solutions containing the lower concentrations of tannic acid appeared generally to reach a state of equilibrium, and manganese concentration leveled off after about 30 days.

A rigorous evaluation of the results in tables 2–5 and in figure 1 is complicated by several factors. The results do indicate, of course, that manganese reduction by the digallic acid takes place and that in most solutions an apparent equilibrium condition was reached. Consideration of the chemical data and the appearance of the solutions during the experiment provide some basis for hypotheses regarding the reactions. If equilibrium is reached, several reactions will be involved. One is the reduction of manganese dioxide, liberating soluble manganese. Divalent manganese was probably produced rather than Mn^{+3} because the more reduced form is the more stable, thermodynamically, and because the colors which developed in the standing samples resembled the ones produced by mixing divalent manganese solutions with digallic acid in the spectrophotometric work. The appearance of these colors suggests that the complexing reaction in which divalent manganese is combined with digallate also must be taken into account. The process of oxidation undoubtedly alters the digallic acid also, but the oxidized material may still be capable of complexing manganese.

Polyethylene is permeable to gases, and diffusion of oxygen and carbon dioxide into the bottles probably took place. The trends in pH observed in solutions containing no tannic acid (table 2) were probably the result of carbon dioxide solution. Eh values for solutions that contained no tannic acid were probably influenced by dissolved oxygen and were not reported because they are probably not related to dissolved manganese.

Solutions listed in table 2 reached very low concentrations of dissolved manganese because very little oxidizable material was present. The solutions at lowest pH did contain some chloride, added in the process of lowering the pH with hydrochloric acid, and some dissolved manganese could have resulted in these solutions from the oxidation of chloride to chlorine. Small amounts of soluble manganese also could have been derived from impurities in the manganese dioxide. The significance of concentrations below 0.10 ppm is somewhat doubtful because the method of determination has low accuracy and precision in that range.

To interpret the results in tables 3–5, the role of the tannic acid is assumed to be to reduce manganese from the Mn^{+4} state to the Mn^{+2} state, and to complex part of the Mn^{+2}. These reactions proceed simultaneously, approaching an equilibrium in which the Eh and pH are those compatible with the activity of Mn^{+2} in the system. In

the earlier stages of the reaction, the Eh probably represents a system involving digallic acid and dissolved oxygen.

In earlier work (Hem, 1963), a series of Eh-pH diagrams were prepared for manganese systems. From these diagrams an equilibrium Eh can be calculated for any activity of dissolved Mn^{+2} and hydrogen ions. Comparison of this calculated Eh with that actually measured gives an indication as to the degree to which equilibrium is reached in the solution. If the calculated Eh is greater than the measured Eh, the solution is unsaturated and is still capable of reducing and dissolving more manganese. If the calculated Eh is less than the measured value, supersaturation with manganese is indicated. This apparent supersaturation could occur in an equilibrium condition as the result of complexing, by which the effective concentration of Mn^{+2} is decreased to produce MnT^{+}, the 1:1 complex with digallate ions. The dissolved manganese determined is a total of all species present. The apparent supersaturation was used to compute percentage of manganese complexed in a few of the solutions listed in table 4, and will be discussed later in this report.

The calculated Eh values in tables 3–5 were obtained from large-scale graphs of Eh, pH, and $[Mn^{+2}]$ based on the Nernst equation and the redox couple $MnO_2c+4H^{+}+2e=Mn^{+2}aq+2H_2O$.

Because the ionic strength of the solutions was generally low, between 10^{-3} and 10^{-4}, an activity coefficient of unity was assumed for Mn^{+2}, except in the solutions which were highest in digallic acid and in manganese, where the activity coefficient for Mn^{+2} was estimated on the basis of the Debye-Hückel law to be 0.8. The error introduced by this treatment is small compared to uncertainties in the measurement of Eh.

Reproducibility of Eh measurements in the solutions containing digallic acid was probably ± 0.02 volt or more. Differences between observed and calculated Eh amounting to more than 0.02 volt in the solutions containing digallic acid may therefore be significant. At constant pH a change of 0.02 volt in Eh is equivalent to a change in manganese activity by a factor of about 2. Hence, the Eh is not a very sensitive indicator of manganese behavior. Some indications of interest, however, can be obtained by comparing observed and calculated Eh values listed in tables 3–5.

The observed Eh values in table 3 were at first considerably below the calculated ones, but later in the experiment the calculated and observed values reached agreement, within 0.02 volt. This apparent equilibrium was reached earlier with the solutions started at a high pH. In general, more than 70 hours was required to reach equilibrium. In all but the one containing the smallest amount of dissolved manganese, the Eh data seem to show consistent supersaturation at

the time of the last observation (1,320 hr). The difference between observed and calculated Eh, however, never reached a value greater than 0.02 volt in any of these solutions.

The data in table 4 represent systems where enough digallic acid was present to bring about more extensive reduction and complexing effects. The calculated and observed Eh values are in approximate agreement at 670 hours. The observations at 1,320 hours show that the amount of manganese in solution is greater than could be explained by assuming only Mn^{+2} ions are present. The solutions were filtered after that series of observations and allowed to stand with no manganese dioxide present until the final set of analyses were made after a total elapsed time of 2,600 hours. All except two of the solutions showed some supersaturation at that time.

Table 5 lists results for the solutions containing 1,000 ppm of tannic acid. The amounts of manganese brought into solution were greater than in corresponding solutions containing lesser amounts of tannic acid. At the two lower pH levels the saturation point had not been reached at 1,320 hours. A later observation on these two solutions did not give a usable value for manganese concentration because the fractions to be used for this purpose were lost and no more solution was left. Equilibrium, however, was probably reached in these solutions between the 1,320- and 2,500-hour observations. The solutions having initial pH's of 6.5 or higher reached apparent equilibrium at 1,320 hours, and indicated supersaturation at 2,500 hours.

The general rend of the data is also indicated by figure 1. The solutions containing lesser amounts of tannic acid gave curves which generally began to level off sooner than the more concentrated solutions. The illustrations also show the increased capacity for reductions of the solutions that had lower initial pH's. Because the graphs represent systems influenced by several variables, they cannot be very rigorously interpreted as indications of reaction rates, but they do show general trends in the establishment of equilibrium in the solutions.

CALCULATION OF AMOUNT OF MANGANESE COMPLEXED

The amount of manganese complexed in these solutions can be calculated from the available data and the stability constant for the 1:1 complex, if certain assumptions are made. The equations required are:

$$\frac{[MnT^{+}]}{[Mn^{+2}][T^{-}]}=10^{3.9}, \tag{5}$$

$$\Sigma[Mn]=[Mn^{+2}]+[MnT^{+}], \tag{6}$$

$$\Sigma[T]=[T^{-}]+[MnT^{+}]+[HT], \tag{7}$$

and

$$\frac{[H^+][T^-]}{[HT]}=10^{-6.0}. \tag{8}$$

All activity coefficients are assumed to be unity, and the initial concentration of digallic acid is used as $\Sigma[T]$. Neither of these assumptions is strictly correct, but for the dilute solutions used in these experiments the effect of activity coefficient corrections would be small. The effect of oxidation on the complexing properties of the digallate ion is not easily evaluated. An amount of digallic acid equivalent to perhaps two tenths of the manganese reduced would be oxidixed, but the oxidized digallate might still be capable of complexing manganese. Refinement of the assumption that the availability of digallate for complexing is not seriously affected by oxidation-reduction reactions seems impracticable. The dissociation constant for digallic acid, $10^{-6.0}$, was estimated in earlier studies (Hem, 1960) and is only approximate.

Simultaneous solution of these equations is possible for any of the sets of observations reported in tables 3–5, and will give values for activity of complexed manganese as well as other dissolved species within the limits imposed by the assumptions. The computation, however, was made for only six observations, reported in table 4, where approximately constant dissolved manganese concentrations had been reached. For the six observations the extent of complex formation can also be estimated by using pH and Eh data.

In samples where measured Eh exceeded the calculated Eh, a situation indicating apparent supersaturation with Mn^{+2}, the activity of Mn^{+2} at equilibrium can be calculated by using measured pH and Eh values and the Nernst equation. The difference between the calculated activity of divalent manganese and the total dissolved manganese concentration determined by analysis can then be assigned to the complexed form. This method of evaluating the complexing effect has a rather low order of accuracy because small differences in Eh can bring about major differences in Mn^{+2} activity. Results of computations by both methods are listed in table 4 in terms of percent of total manganese present as the complex.

The proportion of complexing of the manganese ranged from 46 to 66 percent when calculated from the stability constant of the postulated complex. The degree of complexing calculated from the redox potentials was generally somewhat greater and ranged from 77 to 99 percent. Although the values do not check very closely, agreement is about as good as could be expected in view of the uncertainty in the measured Eh and thus they lend some further support to the value for K_1, the stability constant, which was calculated in this study.

SOLVENT-EXTRACTION EXPERIMENTS

A solvent-extraction technique was used in an attempt to isolate the digallic-manganese complex. The solutions which had stood in contact with solid manganese dioxide long enough to dissolve considerable Mn^{+2} were filtered and portions were extracted in separatory funnels with different organic solvents having low solubility in water. The solvents most effective in removing the color from the solutions containing complexed manganese were butyl and amyl alcohol. Carbon tetrachloride, benzene, xylene, hexane, amyl acetate, 4-methyl propanone, and chloroform all were tried but were not capable of removing either the color or the manganese from the water fraction. Although the butyl and amyl alcohol extractions seemed to remove the colored material, the manganese remained behind the water layer.

The solvent-extraction experiments indicate that the complex does not have a strong enough linkage between the organic molecule and the manganese to survive the extraction, and this approach was abandoned.

STABILITY OF COMPLEX TOWARD OXIDATION

After the digallic acid solutions had attained a maximum concentration of dissolved manganese, a selected group representing different reagent concentrations and starting pH values were filtered through plastic membrane filters with pores 0.45 micron in diameter. Air was bubbled through the samples for 10 hours and they were again filtered and analyzed for manganese. No change in manganese content had occurred. The pH of the samples was then raised to 9.00 with sodium hydroxide and again air was bubbled through them for 10 hours. This time, after filtration, the manganese in solution had decreased by about 10 percent.

In previous experiments (Hem, 1963), rates of oxidation of divalent manganese were measured at pH 9.0. In the absence of sulfate and bicarbonate, one-half of the manganese was oxidized in 1½ minutes. Half times of 60–80 minutes were observed in the presence of sulfate and bicarbonate. Obviously, the reaction is very much slower in the presence of digallic acid.

Experiments were made using solutions of manganese complexed with digallic and gallic acids in which the pH was raised to about 9.5 and was maintained at a selected value. Samples were periodically removed, filtered through a plastic membrane filter, and analyzed for manganese. The results indicated that the rate of loss of manganese attributable to the destruction of the complex by oxidation is appreciable. The half time indicated for pH 9.8 was about 8 hours for the manganese-digallate complex. The stability of the gallic acid complex toward oxidation was similar.

SOLUTION OF MANGANESE DIOXIDE BY GALLIC ACID

A series of equilibrium experiments like the ones used for digallic acid was performed to evaluate the reducing and complexing action of gallic acid on manganese dioxide. Because these organic acids are chemically similar to each other, a less elaborate series of experiments for gallic acid appeared to be reasonable and capable of demonstrating points of similarity or differences in behavior. Accordingly, a series of four 500-ml samples was prepared; two contained 50 ppm and two contained 200 ppm of gallic acid. The pH of one of the 50-ppm gallic acid and that of one of the 200-ppm gallic acid solutions was raised to about 7.75. The other two solutions were not adjusted but were left at the pH near 4.0, reached as a result of the dissociation of the gallic acid. To each solution was added 1.0 g of reagent-grade manganese dioxide. The solutions were allowed to stand in polyethylene bottles, at 25°C, for about 5 months. During this time the pH, Eh, and manganese, which passed through plastic filter membrane with 0.45-μ diameter pores, were measured on three occasions. The results are listed in table 6. The data do not give enough points to prepare graphs but can be compared approximately with the results obtained in experiments with digallic acid.

In the first 18 hours all four solutions reduced some of the manganese and brought it into solution. As was observed in the earlier experiments with digallic acid, the reducing action was stronger at the lower pH, and the strong solution of gallic acid brought more manganese into solution than the weaker one. The observation at 310 hours showed a considerable further increase in dissolved manganese. This dissolution followed the same pattern observed at the end of the first 18 hours. The final observation was made more than 4½ months after the experiment was started and showed a smaller amount of dissolved manganese than the 310-hour measurement. On very long standing it would seem the gallic acid and the complex are destroyed or altered by oxidation by atmospheric oxygen.

The pH of the solutions tended to converge, the final value being above 7.0 and appreciably higher than was noted in solutions of digallic acid.

The calculated values for Eh reported in table 6, as in tables 2–5, are based on the equilibrium involving manganese dioxide and divalent manganese without complexing. Approximate agreement between observed and calculated Eh was obtained at 310 hours, except for one sample which seemed to reach this agreement earlier.

The calculated Eh was considerably less than the observed Eh at the time of the final observation; this fact indicates some degree of

TABLE 6.—*Manganese concentration, pH, and Eh of solutions of gallic acid in contact with manganese dioxide*

Time (hours)	Manganese concentration, pH, and Eh of 50-ppm and 200-ppm gallic acid solutions for the initial pH indicated							
	50 ppm gallic acid							
	Initial pH, 4.1				7.7			
	Mn (ppm)	pH	Eh (volts)		Mn (ppm)	pH	Eh (volts)	
			Observed	Calculated			Observed	Calculated
0	-------	4. 10	0. 49	-------	-------	7. 70	0. 35	-------
18	5. 9	5. 33	. 49	0. 71	3. 2	6. 78	. 44	0. 54
310	13	7. 25	. 46	. 46	8. 0	7. 38	. 47	. 46
3,380	9. 7	7. 80	. 54	. 46	4. 8	7. 45	. 53	. 46
	200 ppm gallic acid							
	3.8				7.8			
	Mn (ppm)	pH	Eh (volts)		Mn (ppm)	pH	Eh (volts)	
			Observed	Calculated			Observed	Calculated
0	-------	3. 80	0. 54	-------	-------	7. 80	0. 32	-------
18	12	4. 38	. 51	0. 81	6. 3	7. 14	. 37	0. 49
310	46	7. 01	. 48	. 48	24	7. 45	. 47	. 44
3,380	39	7. 70	. 52	. 40	17	7. 90	. 50	. 38

supersaturation. If it were assumed that the difference between observed and computed Eh could all be ascribed to effects of complexing of divalent manganese, nearly all the dissolved manganese would be assigned to the complexed form.

The amount of complexing to be expected in these solutions was computed by using equations analogous to the ones used for digallic acid. The stability constant of $10^{2.16}$ for the 1:1 complex (Kachhawaha and Bhattacharaya, 1962) and the first dissociation constant for gallic acid of $10^{-4.40}$ (Lange, 1956) were used. The computations gave a maximum of some 10 percent of total manganese complexed in the solutions containing 50 ppm gallic acid and about 20 percent complexed in the solutions containing 200 ppm gallic acid.

One might assume that the 310-hour observation for the 200-ppm gallic acid solution started at pH 7.8 represents a condition less complicated by oxidation and related alterations that probably affected all the observations at 3,380 hours. If this is assumed then the proportion of manganese complexed calculated from the pH and Eh

data is still close to 90 percent of the total dissolved manganese. The computation based on the reported stability constant indicates that only 13 percent of the manganese is complexed.

Although these computations are inexact and do not seem sufficient for calculating a new stability constant for the manganese-gallate complex, they suggest that the complex is somewhat more stable than the published data would indicate; a value nearer 10^3 would agree more closely with results obtained in this work.

EFFECTS OF GALLIC ACID COMPARED WITH THOSE OF DIGALLIC ACID

Comparison of the results of the experiments with gallic acid and with digallic acid suggests that gallic acid is more effective than digallic acid as a reducing agent, both with respect to the rate of reaction and to the amount of manganese reduced per unit weight of organic acid. However, digallic acid evidently forms a complex with divalent manganese that is more resistant to oxidation than the one formed with gallic acid.

The amount of manganese brought into solution after 18 hours, in solutions containing 50 ppm gallic acid, was greater than amounts in solution after a similar length of time in solutions at similar pH containing 100 ppm or even 1,000 ppm of digallic acid. Upon standing, a loss of manganese was observed in solutions containing gallic acid. This effect was generally absent or less pronounced in solutions containing digallic acid. The more rapid increase in dissolved manganese in early stages of the experiment, and the attainment of higher manganese content per milligram of organic acid originally present when gallic acid was the reducing agent, demonstrate the superiority of gallic acid as a reducing agent. However, the apparent loss of manganese from solution by oxidation and the behavior of gallic acid and manganese in spectrophotometric experiments show that the complexing action of the digallic acid is stronger than that of gallic acid.

IMPORTANCE OF REDUCING AND COMPLEXING IN NATURAL SYSTEMS

As this paper and its three predecessors dealing with the chemistry of manganese in natural water have pointed out, organic factors of various types are frequently important. Except for the water from some thermal springs and water which has been polluted, surface or ground water containing more than 0.10 ppm manganese may well have been affected by these organic factors. For example, the move-

ment of ground water into and out of sediments rich in organic debris provides an excellent mechanism for producing a low Eh, reducing manganese oxides, and retaining the dissolved manganese in solution by complex formation.

Published data on composition of river water give few direct indications of the influence of organic matter in the occurrence of manganese in natural water. One might expect, for example, a positive correlation between manganese content and the amount of organic coloring matter present in river waters, at least in regions where manganese is readily available in the soil. Although only a few data exist for testing this hypothesis, because so few waters have been analyzed for manganese, no strong correlation is indicated. In pools adjacent to the channel of the Cacapon River in West Virginia, Slack (1964) found that increased manganese concentration was due to leaching of leaves which had fallen or were otherwise brought into the pools, and the amount of manganese as well as some other elements was greatest in the most highly colored water. The leaves themselves were probably the source of manganese at this location. The data on composition of river waters of the world collected by Durum, Heidel, and Tison (1960) show no well-defined relation between color intensity of water and manganese content for the whole mass of data, but for some individual streams there is an indication of higher manganese content at times when the water is more highly colored.

Manganese determinations for samples of streams in the Ohio River basin show that frequently the higher manganese concentrations occur in the more highly colored waters, but there are many exceptions to this general trend (U.S. Geol. Survey, 1960), especially in streams where large amounts of manganese are brought in by disposal of industrial waste or by mine drainage.

The principal importance of processes involving organic materials in the occurrence of manganese in natural water is probably in connection with the reduction of manganese oxide. Absorption of manganese from soil by growing plants is no doubt a major factor in making the element available for solution in runoff. The reduction of oxide by organic matter in soil moisture or in the bottom mud of lakes is probably also a common process. It is not difficult to visualize mechanisms by which water might be induced to move from organic-rich environments through zones containing oxidized manganese, as for example in collector wells near streams. The manganese content of water pumped from some wells might thus tend to increase with time.

The aim of the work which has been described was to present in a systematic way a summary of the chemical factors which control the

behavior of manganese in relatively pure natural water at and near the land surface. The behavior of manganese in hydrothermal environments and in brines, or factors which might bring about accumulation of manganese minerals, may be related to some of the topics which have been discussed. These topics, however, represent areas which were not directly investigated.

Most of the theoretical concepts discussed in this series of papers were tested in the laboratory. Field investigations of manganese behavior in ground water, giving particular attention to mineral sources of the element in rocks and soils, and studies of areas where solution and deposition of manganese occur in beds of rivers and creeks would be desirable as a further test of the concepts. Colleagues in the Geological Survey and others who might be able to do so are urged to undertake these studies.

LITERATURE CITED

Bjerrum, Jannik, Schwarzenbach, Gerold and Sillen, L. G., 1957, Stability constants, part 1, Organic ligands: Spec. Pub. no. 6, Chem. Soc. (London), 1957, 105 p.

Black, A. P. and Christman, R. F., 1963a, Characteristics of colored surface waters: Am. Water Works Assoc. Jour., v. 55. p. 753–770.

——— 1963b, Chemical characteristics of fulvic acids: Am. Water Works Assoc. Jour., v. 55, p. 897–912.

Durum, W. H. and Haffty, Joseph, 1963, Implications of the minor element content of some major streams of the world: Geochim. et Cosmochim. Acta, v. 27, p. 1–11.

Durum, W. H., Heidel, S. G. and Tison, L. J., 1960, World-wide runoff of dissolved solids: Pub. 51 Internat. Assoc. of Sci. Hydrology, p. 618–628.

Feitknecht, W., Brunner, P. and Oswald, H. R., 162, Uber den Einfluss der Feuchtigkeit auf die Oxydation von Manganhydroxid durch molecularen Sauerstoff: Zeitschr. anorg. u. allg. Chem., v. 316, p. 154–160.

Frondel, Clifford, 1953, New manganese oxides hydrohausmannite and woodruffite: Am. Mineralogist, v. 38, p. 761–769.

Hem, J. D., 1960, Complexes of ferrous iron with tannic acid: U.S. Geol. Survey Water-Supply Paper 1459–D, p. 75–94.

——— 1963, Chemical equilibria and rates of manganese oxidation: U.S. Geol. Survey Water-Supply Paper 1667–A, 64 p.

Hutchinson, G. E., 1957, Treatise on Limnology: New York, John Wiley & Sons, Geography, Physics and Chemistry, v. 1, 1015 p.

Ingols, R. S. and Wilroy, R. D., 1963, Mechanism of manganese solution in lake waters: Am. Water Works Assoc. Jour., v. 55, p. 282–290.

Kachhawaha, M. S. and Bhattacharya, A. K., 1962, Gallate complex of manganese (II): Indian Acad. Sci. Proc., v. 32a, p. 376–382.

Lamar, W. L. and Goerlitz, D. F., 1963, Characterization of carboxylic acids in unpolluted streams by gas chromatography: Am. Water Works Assoc. Jour., v. 55, p. 797–802.

Lange, N. A., 1956, Handbook of chemistry: Sandusky, Ohio, Handb. Publishers Inc., 1969 p.

Lieth, Helmut, 1963, The role of vegetation in the carbon dioxide content of the atmosphere: Jour. of Geophys. Research, v. 68, p. 3887–3898.

Nygaard, Gunnar, 1953, On the productivity of five Danish waters: Internat. Assoc. of Theoretical and Appl. Limnology Proc., p. 123–132.

Oborn, E. T., 1964, Intracellular and extracellular concentration of manganese and other elements by aquatic organisms: U.S. Geol. Survey Water-Supply Paper 1667–C, 18 p.

Rawson, Jack, 1963, Solution of manganese dioxide by tannic acid: Art. 117 *in* U.S. Geol. Survey Prof. Paper 475–C, p. C218–C219.

Shapiro, Joseph, 1964, Effect of yellow organic acids on iron and other metals in water: Am. Water Works Assoc. Jour., v. 56, p. 1062–1082.

Slack, K. V., 1964, Effect of tree leaves on water quality in the Cacapon River, West Virginia: Art. 161 *in* U.S. Geol. Survey Prof. Paper 475–D, p. D181–D185.

U.S. Geological Survey, 1960, Quality of Surface Waters of the United States, 1957, parts 1–4, North Atlantic Slope Basins to St. Lawrence River Basin: U.S. Geol. Survey Water-Supply Paper 1520, 641 p.

Yoe, J. H. and Jones, A. L., 1944, Colorimetric determination of iron with disodium-1, 2-dihydroxybenzene-3,5,disulfonate: Indus. and Eng. Chem. Anal. Ed., v. 16, p. 111–115.

Reduction and Complexing of Manganese by Gallic Acids

By JOHN D. HEM

CHEMISTRY OF MANGANESE IN NATURAL WATER

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1667-D

Chemical reactions with organic acids which influence the behavior of manganese in natural water

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1965

UNITED STATES DEPARTMENT OF THE INTERIOR

STEWART L. UDALL, *Secretary*

GEOLOGICAL SURVEY

Thomas B. Nolan, *Director*

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 - Price 20 cents (paper cover)

CONTENTS

	Page
Abstract	D1
Introduction	1
Previous work	1
Behavior of manganese in lakes	2
Organic materials in natural water	4
Properties of tannic acid	5
Digallic acid complex with manganese	6
Determination of stability constant	8
Properties of gallic acid	10
Complexes of Mn^{+2} with other organic ligands	11
Complexes with higher oxidation states of manganese	12
Solution of manganese dioxide by digallic acid	13
Calculation of amount of manganese complexed	20
Solvent-extraction experiments	22
Stability of complex toward oxidation	22
Solution of manganese dioxide by gallic acid	23
Effects of gallic acid compared with those of digallic acid	25
Importance of reducing and complexing in natural systems	25
Literature cited	27

ILLUSTRATION

	Page
FIGURE 1. Solution of manganese by tannic acid at (*A*) pH 5.5 and (*B*) pH 8.5	D15

TABLES

	Page
TABLE 1. Computation of stability constant for manganese digallate complex	D9
2. Manganese concentration and pH of solutions in contact with manganese dioxide. Tannic acid absent	14
3–6. Manganese concentration, pH, and Eh of—	
3. 10-ppm tannic acid solution in contact with manganese dioxide	16
4. 100-ppm tannic acid solution in contact with manganese dioxide	16
5. 1,000-ppm tannic acid solution in contact with manganese dioxide	17
6. Solutions of gallic acid in contact with manganese dioxide	24

CHEMISTRY OF MANGANESE IN NATURAL WATER

REDUCTION AND COMPLEXING OF MANGANESE BY GALLIC ACIDS

By JOHN D. HEM

ABSTRACT

Tannic (digallic) and gallic acids form 1:1 complexes with Mn^{+2} in dilute solution. The stability constant of the digallic complex was determined to be $10^{9.9}$ by spectrophotometric studies. Water solutions of tannic and gallic acid can bring 100 parts per million or more of manganese into solution from solid manganese dioxide reagent. The reducing and complexing reactions are most rapid at pH's below 5. The manganese brought into solution was oxidized very slowly at pH's as high as 9.8.

INTRODUCTION

The biochemical factors that are involved in the chemical behavior of manganese in natural environments have been touched upon in the earlier papers in this series. A further study of some chemical reactions that may influence manganese solution and deposition is described here. The study concerns the behavior of oxidized and reduced forms of manganese in the presence of the organic compounds tannic acid and gallic acid. The rates of reduction of tetravalent manganese by the organic acids, and the form and stability of the soluble manganese compounds formed in the reduction process, were investigated. The results provide some indications as to the principles which govern the circulation of manganese in natural environments at or near the land surface, where organic material is plentiful.

PREVIOUS WORK

Preliminary studies of the behavior of divalent manganese in dilute solutions of tannic acid were described by the writer in an earlier report (Hem, 1963, p. A51–A52), but no definite conclusions were drawn. A green color was observed in solutions containing tannic acid and divalent manganese, and a similar color was noted when the

pH of the tannic acid solutions was increased in the absence of manganese. Tannic acid noticeably retarded the rate of oxidation of divalent manganese when the alkaline solutions were exposed to the air. In some environments, such as bogs, that are rich in organic matter, the effects of organic solutes are unquestionably important. In this paper reduction and complexing effects have been studied in detail so that their importance could be intelligently evaluated. Some preliminary results of experiments with tannic-acid reduction of manganese dioxide have been reported by Rawson (1963).

BEHAVIOR OF MANGANESE IN LAKES

One of the more common water-quality problems encountered in the water-supply industry is the appearance of manganese in solution in the water withdrawn from a supply reservoir. The literature contains many references to this type of problem, with descriptions of conditions found and methods used for coping with the problem. The causes, however, have not always been clearly understood or satisfactorily explained.

Vegetation requires manganese in its life processes, and some of the aquatic species of plants seem to accumulate the element (Oborn, 1964). Hutchinson (1957, p. 805) states that the manganese content of lake water is directly related to the productivity of the lake. Lakes and reservoirs support a considerable volume of aquatic vegetation, ranging in size from diatoms to large water weeds rooted in the lake bottom, and during the growing season as much as 10 tons of dry cellulose and related material could be produced per acre of water surface (Lieth, 1963). This high production rate is probably more typical of sewage-oxidation ponds or peat-bog or swamp environments than of a clear lake, but any water impoundment can be expected to produce a considerable mass of organic matter each year. In his studies of productivity in several lakes in Denmark, Nygaard (1953) found a production rate of organic matter of 0.62 g per day per square meter in relatively clear water 28 meters deep. This rate is equivalent to more than a third of a ton per acre in a growing season of 150 days and is probably lower than the usual rate for a storage reservoir. In large part, the organic matter produced in each growing season decays, and a residue of low-solubility material settles to the lake bottom.

Organic matter of aquatic vegetation contains from a few hundredths to a few tenths of a percent of manganese (Oborn, 1964). The amount of manganese present depends partly on its availability. Bottom-rooted plants can extract manganese from the soil below the water surface, but free-floating forms can obtain it only from the water in which they grow.

The quantitative importance of biological productivity as a mechanism for trapping manganese in a lake can be estimated in several ways. The amount of manganese in solution brought into a reservoir during the growing season probably is normally almost all removed biologically. The median manganese concentration of North American rivers of major size is reported by Durum and Haffty (1963) to be 20 micrograms per liter. Thus, in 1 acre-foot of water, one might expect to find about 25 g of manganese. The median concentration of 20 micrograms per liter is equivalent to 0.02 ppm (parts per million) and is a higher concentration than might be expected from the rather sparse data for manganese content in the analytical records published by the U.S. Geological Survey in annual reports on quality of surface water of the United States. In keeping with longstanding custom, the dissolved constituents in river water are ordinarily determined on filtered or clarified samples. Durum and Haffty used samples which had been filtered and acidified, but the filtration did not remove all the particulate matter. Hence, their results may include some of the particulate manganese that was present. Hutchinson (1957) indicates that particulate manganese may be utilized by plants and in any event is likely to be precipitated in a standing water body such as a lake or reservoir.

A production rate of one-quarter ton of dry vegetation per acre of lake surface per year, of material containing 0.10 percent manganese, would represent a rather modest productivity and would require 250 g of manganese per acre of lake surface. The amount of manganese available from lake water having 20 micrograms of manganese pe liter, or 25 g of dissolved manganese per acre-foot, is enough to supply the biochemical demand for the whole year if the photosynthetic process is active to a depth of 10 feet. An annual inflow of water sufficient to renew the manganese supply would be required to maintain the process. Bottom-rooted aquatic species growing in shallow water would extract some of their manganese from the soil of the lake bottom. When the growing season ends, the crop of vegetation dies back and the debris settles toward the bottom of the lake. This debris carries with it at least a part of the manganese originally incorporated in the vegetation and forms an organic-rich precipitate.

Biological processes, therefore, tend to remove manganese from water and transfer it to a lake-bottom precipitate in significant amounts. The normal circulation of aerated water through the lake maintains oxidizing conditions and depresses manganese solubility. During periods of thermal stratification, however, the deeper water may be depleted in oxygen through biochemical processes to a degree that induces reduction and re-solution of manganese in water near the bottom muds that contain the manganese placed there earlier

through the decay of vegetation. The volume of water, so affected, will generally be small compared with the volume from which this manganese was originally extracted. Thus, the effect of a 10-fold or 100-fold concentration could readily be achieved, leading to a manganese concentration in the bottom water of 0.2 ppm or 2.0 ppm instead of 20 micrograms per liter. Concentrations higher than a few tenths parts per million lead to problems if introduced into water distribution systems. Intakes may obtain such water if they are oriented in such a way as to intercept bottom water, or if the bottom water migrates to other levels.

Although the biochemical processes of manganese removal and occasional re-solution can probably account for the usual occurrences of manganese in water of storage reservoirs, the actual processes in the bottom sediments may involve some additional factors related to organic complexing and reduction. In a few areas, such as the piedmont region of Georgia studied by Ingols and Wilroy (1963), the manganese content of the material making up the original bottom of the reservoir may be high enough to be a significant source of manganese for solution.

ORGANIC MATERIALS IN NATURAL WATER

The nature of naturally occurring organic solutes in colored river and lake water has never been completely established, even though such materials have been extensively studied. Lamar and Goerlitz (1963), however, were able to identify 12 carboxylic acids in unpolluted surface water from streams in the States of California and Washington. Substances identified included acetic, propionic, butyric, valeric, caproic, lactic, malonic, maleic, succinic, adipic, fumaric, and oxalic acids. The concentrations observed were from 4 to 592 parts per billion. Other carboxylic acids of higher molecular weight were also isolated but could not be specifically identified by gas chromatography because they were relatively stable and nonvolatile. Such acids have commonly been referred to in the literature as "humic" or "fulvic," or are given other names, which imply a definite chemical formula or structural pattern. Actually these names have been used with various connotations by many different writers to refer to complex mixtures of high molecular weight organic acids and polymers which impart a brown or yellow color to water and can be extracted by certain empirical procedures. The color and probably the structure of these materials are partly a function of pH and it has not been agreed whether they occur in true solution or as a colloidal suspension. The molecules of these substances may actually approach colloidal size.

Shapiro (1964) conducted extensive studies of organic coloring matter which he extracted from lake water which he refers to as

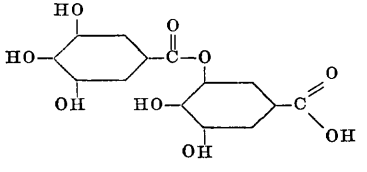
"yellow organic acids" and has determined to be a mixture of aliphatic polyhydroxy carboxylic acids.

Black and Christman (1963a, b) suggested that the organic material responsible for color observed in many natural river waters consists of hydroxycarboxylic acids which have some degree of unsaturation and aromaticity. Their material also contained between 1 and 2 percent nitrogen. Lamar and Goerlitz (1963) reported that the infrared spectrum of colored material obtained from one of their waters resembled that of metadigallic acid, and the studies of Black and Christman (1963b) also indicate that such a compound can be expected in colored natural water. Therefore, it is possible to obtain some useful indications of the behavior of manganese in natural waters by studying the reactions between manganese and digallic (tannic) acid. Tannic acid is readily available in relatively pure form. Another series of experiments was performed with gallic acid, $C_6H_2(OH)_3COOH$, in the expectation that the simpler compound would be more stable and easier to work with.

The results of experiments with well-defined chemical compounds can be expressed in relatively exact terms, with respect to the nature of reactions and products and to the stability of complex ions which are produced. However, results of experiments with the natural organic materials extracted from water are usually less exact.

PROPERTIES OF TANNIC ACID

Tannic acid (digallic acid) has the chemical formula $(HO)_3C_6COO C_6H_2(OH)_2COOH$, and can be represented structurally as



It is formed by hydrolysis from the more complex substances called tannins. Tannins are commonly present in vegetation, and therefore natural water, which usually has some contact with plant debris, commonly contains tannic acid or chemically similar material in solution.

The reagent-grade tannic acid used in this work was a pale yellow-brown powder, which dissolved readily in water. Solutions containing 1 mg of reagent per ml of water were pale yellow, and at this concentration had a pH near 4.0.

In earlier work (Hem, 1960, p. 78) the writer estimated the first dissociation constant for tannic acid to be about 10^{-6}. The curves obtained in potentiometric titrations of the tannic acid with strong base gave no well-defined inflection points but seemed to suggest that

the carboxyl hydrogen is mostly titrated before the phenolic hydrogens are detached from the molecule. The amount of base consumed, however, suggests that some influence from the phenolic hydrogens is probably present at pH 8 and that this influence increases as pH increases.

Redox titrations of tannic acid at various pH's using potassium permanganate and platinum and saturated calomel electrodes were performed to evaluate the reducing ability of the reagent. In these titrations the manganese was at first reduced from Mn^{+7} to Mn^{+2}, but ultimately a black flocculent precipitate, or a dark-brown colloidal suspension, containing Mn^{+4}, was produced. These experiments indicate that solutions of digallic acid are definitely capable of reducing manganese to the Mn^{+2} state, and that their ability for reduction is increased by lowering the pH.

The chemical mechanisms involved in the reduction of permanganate by digallic acid were not definitely ascertained. The color of the solution suggests that the organic compound undergoes considerable alteration in the process. For the present study, the processes of oxidation and reduction which are of interest are those involving Mn^{+2} and Mn^{+4}, and therefore no detailed investigations of the effects of permanganate on digallic acid seemed necessary.

The amount of permanganate which reacted with 10 mg (3.1×10^{-5} moles) of digallic acid without precipitating manganese oxide at pH 7.0 was about 6×10^{-5} moles. The conversion of one MnO_4^- ion to Mn^{+2} involves the gain of five electrons. Hence, the reduction equivalency of digallic acid in the conditions of this particular experiment was about 10 times its molality. One mole of tannic acid, therefore, should be capable of reducing 5 moles of Mn^{+4} to Mn^{+2}.

If, in being oxidized, the digallic acid molecule loses all 5 of its phenolic groups, and they are replaced with hydrogen, the net effect on the nominal charges on the carbon atoms in the 2 benzene rings is equivalent to the loss of 10 electrons. This mechanism would, therefore, be in accord with the results of the permanganate titration.

DIGALLIC ACID COMPLEX WITH MANGANESE

In earlier work (Hem, 1960), digallic acid appeared to form complexes with ferrous iron, and the possibility of similar complex formation with manganous ions was investigated. Aliquots were prepared containing 5.0 mg and 10.0 mg of digallic acid and small amounts of Mn^{+2} ranging from 0.02 to 1.0 mg. These aliquots were adjusted to pH 7.0 with 0.016-molar sodium hydroxide, diluted to 25 ml, and the intensity of the green color which formed was measured with a spectrophotometer after the aliquots stood for 2 hours to

permit complete color development. Maximum absorbance occurred at 400 mμ. A direct linear response was obtained for the lower concentrations of manganese (up to about 0.15 mg of manganese in 25 ml of water). This response indicates a complex, whose behavior was in accord with Beers' law, in dilute solution. As the concentration of manganese was increased, however, a maximum color intensity was reached beyond which further increases in manganese content brought about no change.

The composition of the complex was determined from the spectrophotometric data using the procedure of Yoe and Jones (1944). In this procedure the absorbance is determined for various mole ratios of ligand to manganese. Straight parts of the resulting curve are extrapolated to an intersection which indicates the mole ratio of the predominant complex. A 1:1 mole ratio of manganese and digallic acid was indicated, at least for the concentrations of the reactants used here (about 10^{-4} to 10^{-6} molar) and at a pH near or slightly above neutrality.

The intensity of the green color was a function not only of manganese and digallic acid activities, but also of pH; the rate at which the color developed was also influenced by pH. The color was more intense at pH 8 than at pH 7 and developed more rapidly at the higher pH. After about 2 hours, at pH 7 and pH 8, the color stabilized and did not change significantly during the next 12–16 hours. Some greenish color was observed in solutions of digallic acid without manganese, when made alkaline with sodium hydroxide. The hue in these solutions, however, was somewhat different from that developed when manganese was present, and the intensity was generally much less when manganese was absent.

The color in these solutions is apparently associated with changes of the molecular configuration of the digallic acid. Such changes are probably brought about to some extent by neutralization with strong base which may displace some of the phenolic hydrogens. The fact that the color development is stronger in the presence of manganese and at higher pH's suggests that the two positive charges of the manganese ion are probably attracted both to the carboxyl and phenolic sites on the digallic acid molecule when the hydrogens in these positions are displaced.

If the digallate ligand is attached to the Mn^{+2} cation, both at the carboxyl and phenolic positions, the 1:1 complex would be uncharged. Perhaps this form would become more abundant as the pH is increased. However, in the absence of positive evidence as to the charge of the complex species, a linkage at only one position has been assumed.

DETERMINATION OF STABILITY CONSTANT

The stability constant of the manganous-digallate complex was determined from the spectrophotometric data using the following lines of reasoning:

The digallate ligand, represented by the symbol T^-, is considered to be the form of tannic acid present in the solutions on removal of the carboxyl hydrogen, and possibly one or more of the phenolic hydrogens, as a result of raising the pH. Solutions used in the experiments were about 10^{-4} molar. In media having so low an ionic strength (near 10^{-4}), the ion activity coefficients, represented by the symbol γ, are near unity. The quantities in brackets are ion activities, the C terms are measured concentrations.

The association equilibrium

$$Mn^{+2}+T^-=MnT^+$$

when written in mass-law form is

$$\frac{[MnT^+]}{[Mn^{+2}][T^-]}=K_1, \tag{1}$$

and the constant K_1 is the stability constant for the 1:1 complex. The total amount of manganese present is either in the complexed or uncomplexed form

$$\sum C_{Mn}=\frac{[Mn^{+2}]}{\gamma_{Mn^{+2}}}+\frac{[MnT^+]}{\gamma_{MnT^+}}. \tag{2}$$

The dissociation of digallic acid can be assumed to be very nearly complete at pH 8.0, because the first dissociation constant is near 10^{-6}. Accordingly, the undissociated form can be ignored, and one may equate the total concentration of the ligand present to two forms

$$\sum C_T=\frac{[MnT^+]}{\gamma_{MnT^+}}+\frac{[T^-]}{\gamma_{T^-}}. \tag{3}$$

The optical density observed in the solutions was used as a measure of the amount of manganese complexed. The spectrophotometer readings were adjusted for the effects of absorbance by digallic acid by means of blanks containing no manganese, and the measurements were all made with the same length of light path. Under these conditions, for any given manganese concentration, a maximum optical density can be obtained by increasing the proportion of digallic acid to manganese in the solution. This maximum value represents the point at which essentially all the manganese has been complexed. For solutions containing the same amount of manganese, but not enough

digallic acid to develop the maximum optical density, a lower optical-density value will be observed, and the ratio of total manganese to complexed manganese will follow the relation

$$\frac{\sum C_{Mn}}{C_{MnT}} = \frac{\text{maximum optical density}}{\text{observed optical density}}. \quad (4)$$

Experimental data for seven different laboratory samples are given in table 1. They may be used to provide solutions for equations 1 to 4. In these solutions manganese concentrations ranged from 7.3×10^{-6} to 7.3×10^{-5} molar, and digallic acid concentrations ranged from 1.2×10^{-4} to 6.2×10^{-4} molar. Maximum ionic strength in these solutions was 4.8×10^{-4}. At this ionic strength, all activity coefficients are close to 1.0. Values for γ_{MnT} and for γ_T cannot be readily computed from the Debye-Hückel equation; therefore, they were assumed to be unity. This assumption introduces an error of less than 5 percent into the values for K_1. Values for $\gamma_{Mn^{+2}}$ were obtained from the Debye-Hückel equation—using the concentrations of Mn^{+2}, Cl^-, Na^+, and T^-—without complexing to calculate the ionic strength. The effect of complexing on the ionic strength could have been corrected for by further computation but this was not done because the spectrophotometric data could not be reproduced very closely. Values for K_1 range from 1.4×10^4 to 5.5×10^3. The mean of the seven values is 8.2×10^3 or $10^{3.9}$.

The uncertainties in the experimental data limit the accuracy of the constant. The pH had a considerable effect on the depth and stability of the color developed, and most of the range observed in K_1 values in table 1 can probably be attributed to this factor. The true value of K_1 could be higher or lower than the value calculated here by a factor of 2.

TABLE 1.—*Computation of stability constant for manganese digallate complex*

Sample	Total manganese ΣC_{Mn} (moles per liter)	Total digallic acid ΣC_T (moles per liter)	Absorbence		K_1
			Maximum	Observed	
1	3.6×10^{-5}	2.5×10^{-4}	0.44	0.250	6.4×10^3
2	3.6×10^{-5}	6.2×10^{-4}	.44	.390	1.4×10^4
3	7.3×10^{-5}	2.5×10^{-4}	.88	.48	6.2×10^3
4	7.3×10^{-6}	1.2×10^{-4}	.46	.240	9.6×10^3
5	3.6×10^{-5}	1.2×10^{-4}	.79	.305	6.0×10^3
6	7.3×10^{-5}	1.2×10^{-4}	1.20	.53	9.6×10^3
7	1.5×10^{-5}	1.2×10^{-4}	.55	.212	5.5×10^3
Mean					8.2×10^3

The behavior of ferrous iron in digallic acid solution at pH 5.0 was considered earlier by the writer (Hem, 1960). For an assumed 1:1 complex the stability constant was estimated to be about 10^{13}, based

on the interference of digallic acid with the formation of the pink complex of dipyridyl and ferrous iron.

Ferrous complexes with organic ligands are considerably stronger, as a rule, than the corresponding manganese complexes. However, the difference between the stability constants for manganese and ferrous complexes with digallic acid seems excessive. The composition of the ferrous complex was not determined, and it may be that the simple FeT^+ structure that was assumed is incorrect.

The chemical behavior of the digallic acid reagent used in this series of experiments was not exemplary for exacting quantitative studies. The solutions of the acid were not stable in contact with air and slowly darkened in color on standing. Changes in the molecular configuration and complexing behavior, which might have resulted, were avoided by using freshly prepared solutions. Complexing and neutralization reactions were relatively slow, and the green complex tended to change color after a day or so, probably because of oxidation. The amount of color development and the rate of complexing were strongly influenced by pH. Close agreement of results in successive sets of samples therefore was not always attained.

The strength of the digallic complex suggests that in solutions containing about 10 ppm of digallic acid and a few tenths of a part per million or less of manganese, the manganese would be about 50 percent complexed. Solutions of this kind may occur in rivers and lakes, although the nature of the organic matter in such water is probably not the same as the material studied. Natural coloring matter can be expected to have significant effects both as a reducing agent and as a complexing agent.

PROPERTIES OF GALLIC ACID

Experiments using gallic acid were compared with those using tannic acid. The reagent grade gallic acid used in these experiments was a white powder, having the chemical formula $(HO)_3C_6H_2COOH \cdot H_2O$. The solutions of this material were colorless at first but tended to darken with age. Both gallic and digallic acids seemed to serve as nutrients for fungi which grew luxuriantly in some of the solutions left in the open air. Biological growths, however, were prevented from forming in the solutions used in the actual experiments.

The first dissociation constant for gallic acid is reported to be 4×10^{-5} (Lange, 1956). The acidic properties are therefore stronger than those of digallic acid. Potentiometric titrations, using glass and saturated calomel electrodes, indicated a single well-defined inflection at pH 6.2. The phenolic hydrogen on the gallic acid molecule appears not to be active as a source of protons until the pH has increased

considerably beyond 6.2, but phenolic hydrogens probably become available at about pH 8.

Gallic acid is an effective reducing agent and, like digallic acid, reacts with permanganate ions to yield Mn^{+2}.

In the titration of gallic acid solutions with sodium hydroxide, a green color was observed which increased in intensity when the pH increased. This color probably resulted from the disruption or rearrangement of the gallic acid molecules. A very similar color was observed when gallic acid and manganese solutions were mixed and the pH adjusted. When manganese was present, however, the color appeared more rapidly and at a lower pH. The color developed in the presence of manganese was a more yellowish shade of green.

The nature of the complex formed between gallic acid and divalent manganese has been studied by Kachhawaha and Bhattacharya (1962). These investigators used higher concentrations of reactants and worked at a lower pH than in the work described here, but they did report a green color in some of their solutions. They reported a 1:1 complex whose stability constant is $10^{2.16}$. This compares with the value $10^{3.9}$ for the 1:1 complex of divalent manganese and digallic acid determined in the present experiments.

Observations in the current study indicate that the gallic acid complex is weaker than the digallic complex, although perhaps not as much weaker as the difference between the two constants would indicate. A preliminary series of experiments in which the gallate complex was developed at pH 7 in the presence of different amounts of manganese and gallic acid gave results which indicated the 1:1 association constant was between 10^2 and 10^3. The value of Kachhawaha and Bhattacharya is in the lower part of this range. Hence, refined experimental work to determine the constant more closely was not undertaken.

COMPLEXES OF Mn^{+2} WITH OTHER ORGANIC LIGANDS

The compilation of Bjerrum, Schwarzenbach, and Sillen (1957) includes stability constants for a 1:1 complex of divalent manganese with several other organic acids which may occur in natural water. The acids and constants for the type reaction (where M is the metal ion and L is the organic ligand)

$$M+L=ML$$

are as follows: Oxalic acid, $K=10^{2.55}$–$10^{3.96}$; malonic acid, $K=10^{3.29}$. It would appear that complexes of divalent manganese with the organic ligands likely to occur in natural waters have similar stabilities.

Concentrations of a few tens of parts per million of organic acids would be necessary in order to complex half of the dissolved manganese. Until more information on the concentrations of manganese in natural water is available, the importance of complex formers such as these in influencing the behavior of other solutes cannot be evaluated.

COMPLEXES WITH HIGHER OXIDATION STATES OF MANGANESE

The oxidation state of manganese, which normally is to be expected in natural water, is Mn^{+2}. Thermodynamic data in the literature show that oxidation of the divalent form will normally produce Mn^{+4} (Hem, 1963), and most aqueous species of trivalent manganese which might be formed as intermediate products are unstable. Some organic complexes of trivalent manganese are known, however. For example, complexes of oxalate ions with trivalent manganese are formed at an intermediate stage in the oxidation of oxalate by permanganate in acid solution. The mechanism of this oxidation reaction has been rather extensively studied and several values for stability constants of the oxalate complexes with trivalent manganese are quoted in Bjerrum, Schwarzenbach, and Sillen (1957). Although the complexes are strong in the sense that most trivalent manganese in solution is tied up on the complexes, they are very susceptible to oxidation. The literature is in general agreement that trivalent manganese is unstable in aqueous solution and can be expected to revert either to divalent or to quadrivalent forms. Strictly speaking, an equilibrium model therefore need not consider trivalent species. However, some consideration must always be given to metastability, and the rate of oxidation of divalent manganese was considerably retarded by the organic acids studied in the work here described. Some writers have expressed the view that manganese in natural water may often occur in the trivalent state, presumably either as a metastable complex or perhaps as a colloidal or molecularly dispersed hydroxide.

The solid species of manganese oxide to be expected in natural environments were considered in an earlier paper (Hem, 1963). The standard free-energy values used for that report indicated that the hydroxide $Mn(OH)_3$ was unstable with respect to dehydrated species, but some indication of hydrated partly oxidized forms was found in laboratory studies of oxidation of Mn^{+2} solutions in air. It is possible, however, to assign a mixed-oxide composition to compounds such as Mn_2O_3, which thus becomes $MnO \cdot MnO_2$ or to Mn_3O_4 which becomes $2MnO \cdot MnO_2$.

Studies of some of the manganese oxide precipitates obtained in the laboratory were made by X-ray diffraction methods, and patterns corresponding to hydrohausmannite, a hydrated form of Mn_3O_4, de-

scribed by Frondel (1953) were sometimes obtained. (More recently, Feitknecht, Brunner, and Oswald (1962) have reported that material prepared and termed hydrohausmannite in earlier experiments was actually a mixture of hausmannite and beta MrO(OH).) The bulk of the material was too poorly crystallized to give any X-ray pattern. In some of the digallic and gallic acid solutions containing dissolved manganese, a flocculent black precipitate formed after the solutions had stood for several months in contact with air. This material gave no distinguishable X-ray pattern. Some of the solutions took on a brown color, perhaps owing to some form of complex of partly oxidized manganese, but possibly also explainable as an organic oxidation product, or a colloidal suspension of manganese dioxide. The brown color could be extracted from these solutions with amyl alcohol, which suggests the material was organic and the result of oxidation of the organic acid.

In a series of solvent-extraction experiments, manganese was left behind in the water fraction. The water solutions were clear and colorless, and no precipitates of oxide formed. These facts suggest that the complexed manganese was originally in the Mr^{+2} form. Some additional evidence against higher oxidation states in the complexed manganese is the approximate agreement between the calculations of amounts complexed from the Eh-pH data and the results obtained using the stability constant where the Mn^{+2} state was assumed at the beginning. These calculations and the solvent extraction studies are discussed later in this paper.

This evidence is not complete proof that organic complexes of trivalent manganese do not occur in natural water. Under the conditions of these experiments, however, manganese evidently did not occur in that state.

SOLUTION OF MANGANESE DIOXIDE BY DIGALLIC ACID

The effectiveness of digallic acid as a reducing agent for manganese dioxide was studied in a series of experiments. Solutions containing 10, 100, and 1,000 milligrams per liter of tannic acid reagent were prepared. Six aliquots of each solution were adjusted in pH by using potassium hydroxide or hydrochloric acid, as required, to give a series of 18 solutions having pH's of 4.5, 5.5, 6.5, 7.5, 8.5, and 9.5. About 500 ml of each solution was placed in a polyethylene bottle, and 1.0 g reagent-grade manganese dioxide powder was introduced. In addition to the 18 bottles containing tannic acid solutions, a group of six bottles was prepared containing distilled water, to which was added first enough acid or base to give the desired pH and then manganese dioxide. Air was not excluded from these solutions, owing to the permeability of polyethylene for gases.

769-002—65——3

The solutions were allowed to stand at a temperature of 25°C and, from time to time, portions were removed for determination of pH and of redox potential. At the same time, an aliquot was filtered through a plastic membrane filter having pore diameters of 0.45μ, and analyzed for dissolved manganese using the standard periodate procedure. The bottles were shaken about once a day to keep the contents mixed. The solutions remaining after 2 months were filtered into new bottles, and some further experiments were performed on these portions.

The results of the determinations are given in tables 2–5. Some indication of the nature of the reactions that took place in these solutions can be gained by examination of these data. General trends can be summarized as follows:

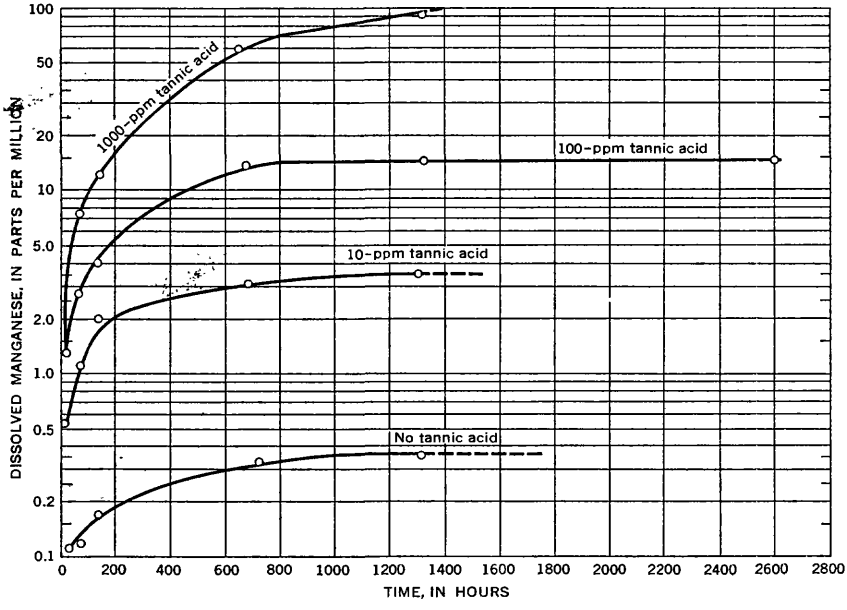
1. Manganese in solution at first increased with time, but tended eventually to reach a stable plateau.
2. More manganese went into solution when the amount of tannic acid was increased.
3. Amounts of manganese dissolved were greatest in solutions that were started at low pH.
4. The solutions containing tannic acid at an initial pH above 7 decreased in pH on standing. The more acid solutions increased in pH. Final pH values were generally between 6.5 and 7.0.
5. The Eh of all the solutions tended generally to increase with time, at first rapidly and then more slowly.
6. Very little manganese was dissolved in the absence of tannic acid.
7. Solutions containing tannic acid and manganese were colored green in the early part of the experiment but later a brown color developed which tended to obscure the original green. The solutions still absorbed light strongly at the wave length used in studies of the complex.

TABLE 2.—*Manganese concentration and pH of solutions in contact with manganese dioxide*

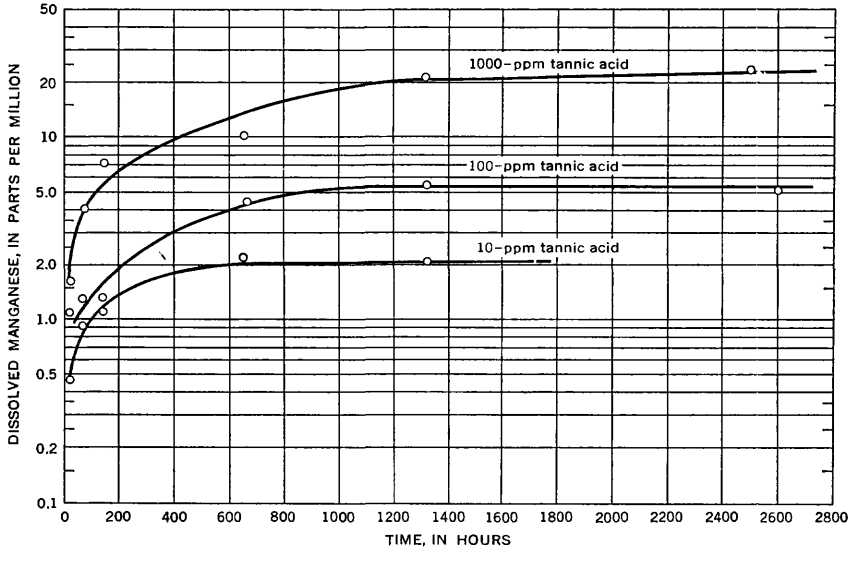
[Tannic acid absent]

Time (hours)	Manganese concentration and pH of solutions in contact with manganese dioxide for the initial pH indicated											
	4.5		5.5		6.5		7.5		8.5		9.5	
	Mn	pH	Mn	pH	Mn	pH	Mn	pH	Mn	pH	Mn	pH
0	0.0	4.50	0.00	5.50	0.00	6.50	0.00	7.50	0.00	8.50	0.00	9.50
3	-----	4.97	-----	5.85	-----	6.48	-----	6.76	-----	6.90	-----	9.08
24	.11	4.85	.11	5.65	.07	6.07	.07	6.59	.03	6.77	.07	8.80
72	.12	4.98	.12	5.72	.07	6.27	.07	6.58	.04	6.69	.04	8.01
144	.24	4.98	.17	5.71	.06	6.20	.06	6.38	.05	6.40	.01	7.00
720	.51	5.20	.33	5.58	.13	5.81	.06	6.20	.06	6.21	.03	6.41
1,320	.61	5.60	.36	5.88	.36	5.43	.08	6.01	.08	6.03	.04	6.32

The rate at which manganese was dissolved is indicated graphically in figure 1 for solutions initially brought to pH 5.5 and pH 8.5. The



A. Initial pH 5.5.



B. Initial pH 8.5.

FIGURE 1.—Solution of manganese from manganese dioxide by different concentrations of tannic acid.

TABLE 3.—*Manganese concentration, pH, and Eh of 10-ppm tannic acid solution in contact with manganese dioxide*

Time (hours)	Manganese concentration, pH, and Eh of 10-ppm tannic acid solution in contact with manganese dioxide for the initial pH indicated																					
	4.5				5.5				6.5				7.5				8.5				9.5			
	Mn (ppm)	pH	Eh (volts)		Mn (ppm)	pH	Eh (volts)		Mn (ppm)	pH	Eh (volts)		Mn (ppm)	pH	Eh (volts)		Mn (ppm)	pH	Eh (volts)		Mn (ppm)	pH	Eh (volts)	
			Observed	Calculated			Observed	Calculated			Observed	Calculated			Observed	Calculated			Observed	Calculated			Observed	Calculated
0	0.0	4.50	------	------	0.0	5.50	------	------	0.0	6.50	------	------	0.0	7.50	------	------	0.0	8.50	------	------	0.0	9.50	------	------
3	------	5.28	0.58	------	------	6.17	0.53	------	------	6.60	0.49	------	------	7.05	0.47	------	------	7.34	0.46	------	------	8.66	0.39	------
21	.64	5.55	.55	0.72	.53	6.10	.52	0.64	.51	6.50	.50	0.60	.47	6.69	.48	0.58	.46	6.93	.50	0.56	.18	8.50	.43	0.37
70	1.1	6.06	.56	.64	1.1	6.39	.55	.60	.88	6.66	.53	.58	.88	6.75	.53	.56	.94	6.70	.55	.52	.24	7.49	.50	.49
142	1.8	6.15	.56	.63	2.0	6.27	.55	.61	1.1	6.42	.53	.60	1.2	6.60	.53	.57	1.1	6.60	.56	.57	.75	6.88	.55	.55
646	3.0	6.14	.61	.62	3.1	6.32	.59	.60	2.0	6.32	.59	.61	1.8	6.55	.59	.58	2.2	6.61	.58	.56	.86	6.80	.58	.56
1,320	3.6	6.19	.60	.62	3.5	6.60	.59	.57	2.4	6.60	.59	.57	1.8	6.59	.58	.57	2.0	6.60	.58	.57	.79	6.70	.56	.57

TABLE 4.—*Manganese concentration, pH, and Eh of 100-ppm tannic acid solution in contact with manganese dioxide*

Time (hours)	Manganese concentration, pH, and Eh of 100-ppm tannic acid solution in contact with manganese dioxide for the initial pH indicated																					
	4.5				5.5				6.5				7.5				8.5				9.5			
	Mn (ppm)	pH	Eh (volts)		Mn (ppm)	pH	Eh (volts)		Mn (ppm)	pH	Eh (volts)		Mn (ppm)	pH	Eh (volts)		Mn (ppm)	pH	Eh (volts)		Mn (ppm)	pH	Eh (volts)	
			Observed	Calculated			Observed	Calculated			Observed	Calculated			Observed	Calculated			Observed	Calculated			Observed	Calculated
0	0.0	4.50	------	------	0.0	5.50	------	------	0.0	6.50	------	------	0.0	7.50	------	------	0.0	8.50	------	------	0.0	9.50	------	------
3	------	5.58	0.54	------	------	6.02	0.52	------	------	6.52	0.49	------	------	7.00	0.49	------	------	7.43	0.48	------	------	8.59	0.41	------
21	1.7	5.83	.52	0.67	1.3	5.98	.53	0.66	1.2	6.30	.51	0.61	1.2	6.42	.52	0.60	1.1	6.79	.51	0.55	.74	7.29	.48	0.50

70	3.2	5.99	.47	.64	2.8	5.98	.48	.64	2.3	6.16	.49	.62	1.6	6.35	.49	.62	1.3	6.57	.49	.58	.88	6.76	.48	.57
142	4.9	5.90	.50	.66	4.2	5.98	.50	.63	3.2	6.00	.50	.64	2.3	6.18	.50	.62	1.3	6.39	.50	.60	1.3	6.75	.50	.56
670	20	6.45	.58	.56	14	6.58	.57	.55	13	6.37	.57	.57	8.7	6.22	.57	.60	4.4	6.40	.57	.59	4.4	6.50	.58	.58
1,320	21	6.87	.56	.50	14	6.78	.57	.52	13	6.91	.56	.50	[4]10	6.91	.58	.51	[5]5.2	6.92	.58	.52	[6]5.2	7.00	.57	.50
2,600	[1]19	6.90	.54	.50	[2]14	6.89	.54	.51	[3]13	6.78	.54	.52	9.3	6.71	.55	.55	5.0	6.79	.54	.54	4.0	6.94	.53	.52

Percentages of manganese as complex, calculated from stability constant and from Eh and pH, respectively, are as follows for the footnoted concentrations:
[1] 46 and 79. [3] 53 and 98. [5] 67 and 99.
[2] 59 and 88. [4] 61 and 99. [6] 66 and 99.

TABLE 5.—*Manganese concentration, pH, and Eh of 1,000-ppm tannic acid solution in contact with manganese dioxide*

Time (hours)	Manganese concentration, pH, and Eh of 1,000-ppm tannic acid solution in contact with manganese dioxide for the initial pH indicated																							
	4.5				5.5				6.5				7.5				8.5				9.5			
			Eh (volts)				Eh (volts)				Eh (volts)				Eh (volts)						Eh (volts)	
	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated	Mn (ppm)	pH	Observed	Calculated
0	0	4.50	------	------	0	5.50	------	------	0	6.50	------	------	0	7.50	------	------	0	8.50	------	------	0	9.50	------	------
3	------	4.88	0.55	------	------	5.88	0.48	------	------	6.49	0.48	------	------	7.12	0.48	------	------	8.29	0.43	------	------	9.16	0.36	------
24	3.6	5.12	.55	0.74	1.3	5.70	.51	0.69	1.2	5.96	.51	0.65	1.8	6.58	.49	0.57	1.6	7.67	.45	0.44	.66	8.40	.41	0.37
72	8.4	5.50	.51	.68	7.3	5.5	.53	.70	2.2	5.66	.54	.68	2.2	6.09	.53	.63	4.0	6.88	.49	.53	.80	7.41	.46	.48
144	15	5.57	.51	.67	12	5.57	.53	.67	7.1	5.75	.53	.66	2.4	6.08	.54	.63	7.2	6.49	.53	.57	1.0	6.69	.51	.57
646	71	5.58	.47	.65	59	5.65	.49	.65	50	5.99	.51	.60	32	6.02	.51	.61	9.8	6.28	.51	.59	3.2	6.47	.51	.60
1,320	112	6.35	.51	.54	90	6.25	.52	.57	80	6.40	.54	.55	54	6.40	.55	.55	21	6.62	.54	.55	15	6.75	.53	.52
2,500	------	6.68	.54	------	------	6.59	.54	------	89	6.68	.55	.52	59	6.67	.56	.53	23	6.90	.56	.53	22	6.78	.55	.51

solutions containing the lower concentrations of tannic acid appeared generally to reach a state of equilibrium, and manganese concentration leveled off after about 30 days.

A rigorous evaluation of the results in tables 2–5 and in figure 1 is complicated by several factors. The results do indicate, of course, that manganese reduction by the digallic acid takes place and that in most solutions an apparent equilibrium condition was reached. Consideration of the chemical data and the appearance of the solutions during the experiment provide some basis for hypotheses regarding the reactions. If equilibrium is reached, several reactions will be involved. One is the reduction of manganese dioxide, liberating soluble manganese. Divalent manganese was probably produced rather than Mn^{+3} because the more reduced form is the more stable, thermodynamically, and because the colors which developed in the standing samples resembled the ones produced by mixing divalent manganese solutions with digallic acid in the spectrophotometric work. The appearance of these colors suggests that the complexing reaction in which divalent manganese is combined with digallate also must be taken into account. The process of oxidation undoubtedly alters the digallic acid also, but the oxidized material may still be capable of complexing manganese.

Polyethylene is permeable to gases, and diffusion of oxygen and carbon dioxide into the bottles probably took place. The trends in pH observed in solutions containing no tannic acid (table 2) were probably the result of carbon dioxide solution. Eh values for solutions that contained no tannic acid were probably influenced by dissolved oxygen and were not reported because they are probably not related to dissolved manganese.

Solutions listed in table 2 reached very low concentrations of dissolved manganese because very little oxidizable material was present. The solutions at lowest pH did contain some chloride, added in the process of lowering the pH with hydrochloric acid, and some dissolved manganese could have resulted in these solutions from the oxidation of chloride to chlorine. Small amounts of soluble manganese also could have been derived from impurities in the manganese dioxide. The significance of concentrations below 0.10 ppm is somewhat doubtful because the method of determination has low accuracy and precision in that range.

To interpret the results in tables 3–5, the role of the tannic acid is assumed to be to reduce manganese from the Mn^{+4} state to the Mn^{+2} state, and to complex part of the Mn^{+2}. These reactions proceed simultaneously, approaching an equilibrium in which the Eh and pH are those compatible with the activity of Mn^{+2} in the system. In

the earlier stages of the reaction, the Eh probably represents a system involving digallic acid and dissolved oxygen.

In earlier work (Hem, 1963), a series of Eh-pH diagrams were prepared for manganese systems. From these diagrams an equilibrium Eh can be calculated for any activity of dissolved Mn^{+2} and hydrogen ions. Comparison of this calculated Eh with that actually measured gives an indication as to the degree to which equilibrium is reached in the solution. If the calculated Eh is greater than the measured Eh, the solution is unsaturated and is still capable of reducing and dissolving more manganese. If the calculated Eh is less than the measured value, supersaturation with manganese is indicated. This apparent supersaturation could occur in an equilibrium condition as the result of complexing, by which the effective concentration of Mn^{+2} is decreased to produce MnT^{+}, the 1:1 complex with digallate ions. The dissolved manganese determined is a total of all species present. The apparent supersaturation was used to compute percentage of manganese complexed in a few of the solutions listed in table 4, and will be discussed later in this report.

The calculated Eh values in tables 3–5 were obtained from large-scale graphs of Eh, pH, and $[Mn^{+2}]$ based on the Nernst equation and the redox couple $MnO_2c+4H^{+}+2e=Mn^{+2}aq+2H_2O$.

Because the ionic strength of the solutions was generally low, between 10^{-3} and 10^{-4}, an activity coefficient of unity was assumed for Mn^{+2}, except in the solutions which were highest in digallic acid and in manganese, where the activity coefficient for Mn^{+2} was estimated on the basis of the Debye-Hückel law to be 0.8. The error introduced by this treatment is small compared to uncertainties in the measurement of Eh.

Reproducibility of Eh measurements in the solutions containing digallic acid was probably ± 0.02 volt or more. Differences between observed and calculated Eh amounting to more than 0.02 volt in the solutions containing digallic acid may therefore be significant. At constant pH a change of 0.02 volt in Eh is equivalent to a change in manganese activity by a factor of about 2. Hence, the Eh is not a very sensitive indicator of manganese behavior. Some indications of interest, however, can be obtained by comparing observed and calculated Eh values listed in tables 3–5.

The observed Eh values in table 3 were at first considerably below the calculated ones, but later in the experiment the calculated and observed values reached agreement, within 0.02 volt. This apparent equilibrium was reached earlier with the solutions started at a high pH. In general, more than 70 hours was required to reach equilibrium. In all but the one containing the smallest amount of dissolved manganese, the Eh data seem to show consistent supersaturation at

the time of the last observation (1,320 hr). The difference between observed and calculated Eh, however, never reached a value greater than 0.02 volt in any of these solutions.

The data in table 4 represent systems where enough digallic acid was present to bring about more extensive reduction and complexing effects. The calculated and observed Eh values are in approximate agreement at 670 hours. The observations at 1,320 hours show that the amount of manganese in solution is greater than could be explained by assuming only Mn^{+2} ions are present. The solutions were filtered after that series of observations and allowed to stand with no manganese dioxide present until the final set of analyses were made after a total elapsed time of 2,600 hours. All except two of the solutions showed some supersaturation at that time.

Table 5 lists results for the solutions containing 1,000 ppm of tannic acid. The amounts of manganese brought into solution were greater than in corresponding solutions containing lesser amounts of tannic acid. At the two lower pH levels the saturation point had not been reached at 1,320 hours. A later observation on these two solutions did not give a usable value for manganese concentration because the fractions to be used for this purpose were lost and no more solution was left. Equilibrium, however, was probably reached in these solutions between the 1,320- and 2,500-hour observations. The solutions having initial pH's of 6.5 or higher reached apparent equilibrium at 1,320 hours, and indicated supersaturation at 2,500 hours.

The general rend of the data is also indicated by figure 1. The solutions containing lesser amounts of tannic acid gave curves which generally began to level off sooner than the more concentrated solutions. The illustrations also show the increased capacity for reductions of the solutions that had lower initial pH's. Because the graphs represent systems influenced by several variables, they cannot be very rigorously interpreted as indications of reaction rates, but they do show general trends in the establishment of equilibrium in the solutions.

CALCULATION OF AMOUNT OF MANGANESE COMPLEXED

The amount of manganese complexed in these solutions can be calculated from the available data and the stability constant for the 1:1 complex, if certain assumptions are made. The equations required are:

$$\frac{[MnT^{+}]}{[Mn^{+2}][T^{-}]}=10^{3.9}, \tag{5}$$

$$\Sigma[Mn]=[Mn^{+2}]+[MnT^{+}], \tag{6}$$

$$\Sigma[T]=[T^{-}]+[MnT^{+}]+[HT], \tag{7}$$

and

$$\frac{[H^+][T^-]}{[HT]}=10^{-6.0}. \quad (8)$$

All activity coefficients are assumed to be unity, and the initial concentration of digallic acid is used as $\Sigma[T]$. Neither of these assumptions is strictly correct, but for the dilute solutions used in these experiments the effect of activity coefficient corrections would be small. The effect of oxidation on the complexing properties of the digallate ion is not easily evaluated. An amount of digallic acid equivalent to perhaps two tenths of the manganese reduced would be oxidixed, but the oxidized digallate might still be capable of complexing manganese. Refinement of the assumption that the availability of digallate for complexing is not seriously affected by oxidation-reduction reactions seems impracticable. The dissociation constant for digallic acid, $10^{-6.0}$, was estimated in earlier studies (Hem, 1960) and is only approximate.

Simultaneous solution of these equations is possible for any of the sets of observations reported in tables 3–5, and will give values for activity of complexed manganese as well as other dissolved species within the limits imposed by the assumptions. The computation, however, was made for only six observations, reported in table 4, where approximately constant dissolved manganese concentrations had been reached. For the six observations the extent of complex formation can also be estimated by using pH and Eh data.

In samples where measured Eh exceeded the calculated Eh, a situation indicating apparent supersaturation with Mn^{+2}, the activity of Mn^{+2} at equilibrium can be calculated by using measured pH and Eh values and the Nernst equation. The difference between the calculated activity of divalent manganese and the total dissolved manganese concentration determined by analysis can then be assigned to the complexed form. This method of evaluating the complexing effect has a rather low order of accuracy because small differences in Eh can bring about major differences in Mn^{+2} activity. Results of computations by both methods are listed in table 4 in terms of percent of total manganese present as the complex.

The proportion of complexing of the manganese ranged from 46 to 66 percent when calculated from the stability constant of the postulated complex. The degree of complexing calculated from the redox potentials was generally somewhat greater and ranged from 77 to 99 percent. Although the values do not check very closely, agreement is about as good as could be expected in view of the uncertainty in the measured Eh and thus they lend some further support to the value for K_1, the stability constant, which was calculated in this study.

SOLVENT-EXTRACTION EXPERIMENTS

A solvent-extraction technique was used in an attempt to isolate the digallic-manganese complex. The solutions which had stood in contact with solid manganese dioxide long enough to dissolve considerable Mn^{+2} were filtered and portions were extracted in separatory funnels with different organic solvents having low solubility in water. The solvents most effective in removing the color from the solutions containing complexed manganese were butyl and amyl alcohol. Carbon tetrachloride, benzene, xylene, hexane, amyl acetate, 4-methyl propanone, and chloroform all were tried but were not capable of removing either the color or the manganese from the water fraction. Although the butyl and amyl alcohol extractions seemed to remove the colored material, the manganese remained behind the water layer.

The solvent-extraction experiments indicate that the complex does not have a strong enough linkage between the organic molecule and the manganese to survive the extraction, and this approach was abandoned.

STABILITY OF COMPLEX TOWARD OXIDATION

After the digallic acid solutions had attained a maximum concentration of dissolved manganese, a selected group representing different reagent concentrations and starting pH values were filtered through plastic membrane filters with pores 0.45 micron in diameter. Air was bubbled through the samples for 10 hours and they were again filtered and analyzed for manganese. No change in manganese content had occurred. The pH of the samples was then raised to 9.00 with sodium hydroxide and again air was bubbled through them for 10 hours. This time, after filtration, the manganese in solution had decreased by about 10 percent.

In previous experiments (Hem, 1963), rates of oxidation of divalent manganese were measured at pH 9.0. In the absence of sulfate and bicarbonate, one-half of the manganese was oxidized in 1½ minutes. Half times of 60–80 minutes were observed in the presence of sulfate and bicarbonate. Obviously, the reaction is very much slower in the presence of digallic acid.

Experiments were made using solutions of manganese complexed with digallic and gallic acids in which the pH was raised to about 9.5 and was maintained at a selected value. Samples were periodically removed, filtered through a plastic membrane filter, and analyzed for manganese. The results indicated that the rate of loss of manganese attributable to the destruction of the complex by oxidation is appreciable. The half time indicated for pH 9.8 was about 8 hours for the manganese-digallate complex. The stability of the gallic acid complex toward oxidation was similar.

SOLUTION OF MANGANESE DIOXIDE BY GALLIC ACID

A series of equilibrium experiments like the ones used for digallic acid was performed to evaluate the reducing and complexing action of gallic acid on manganese dioxide. Because these organic acids are chemically similar to each other, a less elaborate series of experiments for gallic acid appeared to be reasonable and capable of demonstrating points of similarity or differences in behavior. Accordingly, a series of four 500-ml samples was prepared; two contained 50 ppm and two contained 200 ppm of gallic acid. The pH of one of the 50-ppm gallic acid and that of one of the 200-ppm gallic acid solutions was raised to about 7.75. The other two solutions were not adjusted but were left at the pH near 4.0, reached as a result of the dissociation of the gallic acid. To each solution was added 1.0 g of reagent-grade manganese dioxide. The solutions were allowed to stand in polyethylene bottles, at 25°C, for about 5 months. During this time the pH, Eh, and manganese, which passed through plastic filter membrane with 0.45-μ diameter pores, were measured on three occasions. The results are listed in table 6. The data do not give enough points to prepare graphs but can be compared approximately with the results obtained in experiments with digallic acid.

In the first 18 hours all four solutions reduced some of the manganese and brought it into solution. As was observed in the earlier experiments with digallic acid, the reducing action was stronger at the lower pH, and the strong solution of gallic acid brought more manganese into solution than the weaker one. The observation at 310 hours showed a considerable further increase in dissolved manganese. This dissolution followed the same pattern observed at the end of the first 18 hours. The final observation was made more than 4½ months after the experiment was started and showed a smaller amount of dissolved manganese than the 310-hour measurement. On very long standing it would seem the gallic acid and the complex are destroyed or altered by oxidation by atmospheric oxygen.

The pH of the solutions tended to converge, the final value being above 7.0 and appreciably higher than was noted in solutions of digallic acid.

The calculated values for Eh reported in table 6, as in tables 2–5, are based on the equilibrium involving manganese dioxide and divalent manganese without complexing. Approximate agreement between observed and calculated Eh was obtained at 310 hours, except for one sample which seemed to reach this agreement earlier.

The calculated Eh was considerably less than the observed Eh at the time of the final observation; this fact indicates some degree of

TABLE 6.—*Manganese concentration, pH, and Eh of solutions of gallic acid in contact with manganese dioxide*

Time (hours)	Manganese concentration, pH, and Eh of 50-ppm and 200-ppm gallic acid solutions for the initial pH indicated							
	50 ppm gallic acid							
	Initial pH, 4.1				7.7			
	Mn (ppm)	pH	Eh (volts)		Mn (ppm)	pH	Eh (volts)	
			Observed	Calculated			Observed	Calculated
0	-------	4. 10	0. 49	-------	-------	7. 70	0. 35	-------
18	5. 9	5. 33	. 49	0. 71	3. 2	6. 78	. 44	0. 54
310	13	7. 25	. 46	. 46	8. 0	7. 38	. 47	. 46
3,380	9. 7	7. 80	. 54	. 46	4. 8	7. 45	. 53	. 46
	200 ppm gallic acid							
	3.8				7.8			
	Mn (ppm)	pH	Eh (volts)		Mn (ppm)	pH	Eh (volts)	
			Observed	Calculated			Observed	Calculated
0	-------	3. 80	0. 54	-------	-------	7. 80	0. 32	-------
18	12	4. 38	. 51	0. 81	6. 3	7. 14	. 37	0. 49
310	46	7. 01	. 48	. 48	24	7. 45	. 47	. 44
3,380	39	7. 70	. 52	. 40	17	7. 90	. 50	. 38

supersaturation. If it were assumed that the difference between observed and computed Eh could all be ascribed to effects of complexing of divalent manganese, nearly all the dissolved manganese would be assigned to the complexed form.

The amount of complexing to be expected in these solutions was computed by using equations analogous to the ones used for digallic acid. The stability constant of $10^{2.16}$ for the 1:1 complex (Kachhawaha and Bhattacharaya, 1962) and the first dissociation constant for gallic acid of $10^{-4.40}$ (Lange, 1956) were used. The computations gave a maximum of some 10 percent of total manganese complexed in the solutions containing 50 ppm gallic acid and about 20 percent complexed in the solutions containing 200 ppm gallic acid.

One might assume that the 310-hour observation for the 200-ppm gallic acid solution started at pH 7.8 represents a condition less complicated by oxidation and related alterations that probably affected all the observations at 3,380 hours. If this is assumed then the proportion of manganese complexed calculated from the pH and Eh

data is still close to 90 percent of the total dissolved manganese. The computation based on the reported stability constant indicates that only 13 percent of the manganese is complexed.

Although these computations are inexact and do not seem sufficient for calculating a new stability constant for the manganese-gallate complex, they suggest that the complex is somewhat more stable than the published data would indicate; a value nearer 10^3 would agree more closely with results obtained in this work.

EFFECTS OF GALLIC ACID COMPARED WITH THOSE OF DIGALLIC ACID

Comparison of the results of the experiments with gallic acid and with digallic acid suggests that gallic acid is more effective than digallic acid as a reducing agent, both with respect to the rate of reaction and to the amount of manganese reduced per unit weight of organic acid. However, digallic acid evidently forms a complex with divalent manganese that is more resistant to oxidation than the one formed with gallic acid.

The amount of manganese brought into solution after 18 hours, in solutions containing 50 ppm gallic acid, was greater than amounts in solution after a similar length of time in solutions at similar pH containing 100 ppm or even 1,000 ppm of digallic acid. Upon standing, a loss of manganese was observed in solutions containing gallic acid. This effect was generally absent or less pronounced in solutions containing digallic acid. The more rapid increase in dissolved manganese in early stages of the experiment, and the attainment of higher manganese content per milligram of organic acid originally present when gallic acid was the reducing agent, demonstrate the superiority of gallic acid as a reducing agent. However, the apparent loss of manganese from solution by oxidation and the behavior of gallic acid and manganese in spectrophotometric experiments show that the complexing action of the digallic acid is stronger than that of gallic acid.

IMPORTANCE OF REDUCING AND COMPLEXING IN NATURAL SYSTEMS

As this paper and its three predecessors dealing with the chemistry of manganese in natural water have pointed out, organic factors of various types are frequently important. Except for the water from some thermal springs and water which has been polluted, surface or ground water containing more than 0.10 ppm manganese may well have been affected by these organic factors. For example, the move-

ment of ground water into and out of sediments rich in organic debris provides an excellent mechanism for producing a low Eh, reducing manganese oxides, and retaining the dissolved manganese in solution by complex formation.

Published data on composition of river water give few direct indications of the influence of organic matter in the occurrence of manganese in natural water. One might expect, for example, a positive correlation between manganese content and the amount of organic coloring matter present in river waters, at least in regions where manganese is readily available in the soil. Although only a few data exist for testing this hypothesis, because so few waters have been analyzed for manganese, no strong correlation is indicated. In pools adjacent to the channel of the Cacapon River in West Virginia, Slack (1964) found that increased manganese concentration was due to leaching of leaves which had fallen or were otherwise brought into the pools, and the amount of manganese as well as some other elements was greatest in the most highly colored water. The leaves themselves were probably the source of manganese at this location. The data on composition of river waters of the world collected by Durum, Heidel, and Tison (1960) show no well-defined relation between color intensity of water and manganese content for the whole mass of data, but for some individual streams there is an indication of higher manganese content at times when the water is more highly colored.

Manganese determinations for samples of streams in the Ohio River basin show that frequently the higher manganese concentrations occur in the more highly colored waters, but there are many exceptions to this general trend (U.S. Geol. Survey, 1960), especially in streams where large amounts of manganese are brought in by disposal of industrial waste or by mine drainage.

The principal importance of processes involving organic materials in the occurrence of manganese in natural water is probably in connection with the reduction of manganese oxide. Absorption of manganese from soil by growing plants is no doubt a major factor in making the element available for solution in runoff. The reduction of oxide by organic matter in soil moisture or in the bottom mud of lakes is probably also a common process. It is not difficult to visualize mechanisms by which water might be induced to move from organic-rich environments through zones containing oxidized manganese, as for example in collector wells near streams. The manganese content of water pumped from some wells might thus tend to increase with time.

The aim of the work which has been described was to present in a systematic way a summary of the chemical factors which control the

behavior of manganese in relatively pure natural water at and near the land surface. The behavior of manganese in hydrothermal environments and in brines, or factors which might bring about accumulation of manganese minerals, may be related to some of the topics which have been discussed. These topics, however, represent areas which were not directly investigated.

Most of the theoretical concepts discussed in this series of papers were tested in the laboratory. Field investigations of manganese behavior in ground water, giving particular attention to mineral sources of the element in rocks and soils, and studies of areas where solution and deposition of manganese occur in beds of rivers and creeks would be desirable as a further test of the concepts. Colleagues in the Geological Survey and others who might be able to do so are urged to undertake these studies.

LITERATURE CITED

Bjerrum, Jannik, Schwarzenbach, Gerold and Sillen, L. G., 1957, Stability constants, part 1, Organic ligands: Spec. Pub. no. 6, Chem. Soc. (London), 1957, 105 p.

Black, A. P. and Christman, R. F., 1963a, Characteristics of colored surface waters: Am. Water Works Assoc. Jour., v. 55. p. 753–770.

——— 1963b, Chemical characteristics of fulvic acids: Am. Water Works Assoc. Jour., v. 55, p. 897–912.

Durum, W. H. and Haffty, Joseph, 1963, Implications of the minor element content of some major streams of the world: Geochim. et Cosmochim. Acta, v. 27, p. 1–11.

Durum, W. H., Heidel, S. G. and Tison, L. J., 1960, World-wide runoff of dissolved solids: Pub. 51 Internat. Assoc. of Sci. Hydrology, p. 618–628.

Feitknecht, W., Brunner, P. and Oswald, H. R., 162, Uber den Einfluss der Feuchtigkeit auf die Oxydation von Manganhydroxid durch molecularen Sauerstoff: Zeitschr. anorg. u. allg. Chem., v. 316, p. 154–160.

Frondel, Clifford, 1953, New manganese oxides hydrohausmannite and woodruffite: Am. Mineralogist, v. 38, p. 761–769.

Hem, J. D., 1960, Complexes of ferrous iron with tannic acid: U.S. Geol. Survey Water-Supply Paper 1459–D, p. 75–94.

——— 1963, Chemical equilibria and rates of manganese oxidation: U.S. Geol. Survey Water-Supply Paper 1667–A, 64 p.

Hutchinson, G. E., 1957, Treatise on Limnology: New York, John Wiley & Sons, Geography, Physics and Chemistry, v. 1, 1015 p.

Ingols, R. S. and Wilroy, R. D., 1963, Mechanism of manganese solution in lake waters: Am. Water Works Assoc. Jour., v. 55, p. 282–290.

Kachhawaha, M. S. and Bhattacharya, A. K., 1962, Gallate complex of manganese (II): Indian Acad. Sci. Proc., v. 32a, p. 376–382.

Lamar, W. L. and Goerlitz, D. F., 1963, Characterization of carboxylic acids in unpolluted streams by gas chromatography: Am. Water Works Assoc. Jour., v. 55, p. 797–802.

Lange, N. A., 1956, Handbook of chemistry: Sandusky, Ohio, Handb. Publishers Inc., 1969 p.

Lieth, Helmut, 1963, The role of vegetation in the carbon dioxide content of the atmosphere: Jour. of Geophys. Research, v. 68, p. 3887–3898.