Chemistry of Iron in Natural Water

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By J. D. HEM *and* W. H. CROPPER

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CHEMISTRY OF IRON IN NATURAL WATER

SURVEY OF FERROUS-FERRIC CHEMICAL EQUILIBRIA AND REDOX POTENTIALS

By J. D. HEM and W. H. CROPPER

ABSTRACT

Amounts of iron in solution in natural water at equilibrium are related to the pH and Eh of the solution. Important ionic species present include Fe^{+++}, $FeOH^{++}$, $Fe(OH)^{+}_{2}$, Fe^{++}, and $FeOH^{+}$. A stability field diagram shows the Eh and pH values at which each of these predominates. $Fe(OH)_3(aq)$ may be present as part of the dissolved iron in natural water at alkaline pH, and $Fe(OH)_2(aq)$ may exist at pH 10 and above. The total solubility of iron at pH levels from 4 to 9 is shown graphically by seven curves for Eh values from -0.10 to $+0.50$. The amounts of iron that theoretically could be present in solution are mostly below 0.01 ppm if pH is between 5 and 8, and Eh between 0.30 and 0.50. The content of Fe^{++} could exceed 100 ppm, however, at ph 5 and Eh 0.30.

Solutions containing 12 to 24 ppm of iron in various proportions of Fe^{++} to Fe^{+++} were unstable when exposed to air. Changes in the Eh values of these solutions, measured with the platinum and calomel electrodes, indicate that equilibrium is not reached in such mixtures at the end of a week when the initial pH is 3.6 to 4.1.

A natural ground water containing 16 ppm of ferrous iron when collected, and 9 artificial solutions containing from about 12 to about 26 ppm of ferrous iron at pH 5.8 to 6.7, lost iron by oxidation and precipitation of ferric hydroxide at a rate governed by the diffusion of oxygen through the water. An aliquot of the natural water, acidified to pH 1.6, lost no ferrous iron after 3 months.

If equilibrium is assumed in ground water in its natural environment, determinations of pH in the field and of iron concentration in samples of the water form a basis for computing the Eh within aquifers where this property cannot be measured directly.

In aerated waters whose pH is above about 5, ferric iron can be present in excess of 0.01 ppm only as a suspension of oxide or hydroxide. The particles may be of colloidal size or larger. Complexing effects of chloride and fluoride are important in strongly acid solutions of ferric iron, but they do not seem to have much effect on the behavior of iron in waters in the range of pH 5 to 8. Organic complexing effects were not studied.

INTRODUCTION

This report covers a preliminary phase of research by the Geological Survey into the chemistry of iron in natural waters. The report provides a brief introduction to theoretical aspects of dilute aqueous solutions that contain iron, affords a basis for better understanding of the chemical principles which control such solutions, and illustrates the use of theory to explain observed characteristics of natural water.

The results of further research on the occurrence of iron in water will be covered in additional reports. The laboratory work and the interpretation in this report were done in the Water Resources Division research laboratory, Denver, Colo., under the general supervision of S. K. Love, chief, Quality of Water Branch.

The manuscript was reviewed by colleagues of the authors in the Geological Survey, and by others. Especially helpful suggestions were furnished by Prof. R. M. Garrels, Harvard University.

GENERAL FEATURES OF IRON CHEMISTRY

Iron is relatively abundant in the earth's crust. Rankama and Sahama (1950) report that in igneous rocks the only metal more abundant than iron is aluminum. In this discussion, we are concerned only indirectly with the solid-state occurrence of iron in rocks. The element is a principal constituent of many igneous rocks, especially those containing basic silicate minerals. Divalent iron links the chains of silicon-oxygen tetrahedra in minerals such as pyroxenes and amphiboles and links individual tetrahedra in the structure of fayalite. Trivalent iron replaces aluminum in a few silicate minerals. Iron is common also in the form of oxide and sulfide.

Sedimentary rocks contain iron in various forms, but ferric oxides are perhaps the more common. Geochemical data show that iron weathered out of solid minerals is not long retained in solution in water but is redeposited in solid oxides or hydroxides. This research is concerned primarily with the behavior of iron in solution.

Iron occurs in two oxidation states, the divalent or ferrous form and the trivalent or ferric form. Iron in aqueous solution is subject to hydrolysis. The iron hydroxides formed in these reactions, especially the ferric form, have very low solubility. The retention of iron in solution is consequently affected by the pH of the solution. In most natural waters, the pH is not low enough to prevent hydroxides from forming, and under oxidizing conditions, practically all the iron is precipitated as ferric hydroxide.

Another important feature of the chemical behavior of iron in solution is its tendency to form complex ions with inorganic as well as with organic material. These ions may be considerably more stable than the uncomplexed iron and more may remain in solution that might otherwise be the case.

THEORETICAL APPROACH TO IRON CHEMISTRY

FORM OF IRON IN SOLUTION

The most common species of ferric iron in natural waters is ferric hydroxide, $Fe(OH)_3$ (or more correctly, $Fe_2O_3 \cdot 3H_2O$). At equilibrium in the pH range of 5 to 8, this compound is largely in the solid state, the solubility being very low. Relatively stable colloidal suspensions of $Fe(OH)_3$ can exist in much of this pH range, as will be discussed later. Ferric hydroxide is a weak base and ionizes as $Fe(OH)_2^+$, FeO^+, $FeOH^{++}$, and Fe^{+++}. If the pH is sufficiently high, anions such as ferrite, FeO_2^-, are formed. Higher oxidation states are also possible, FeO_4^{--} being the best known of these species. Ferric iron is a powerful former of complexes. The inorganic complexes most likely to be found in natural waters are those formed with chloride, fluoride, phosphate, sulfate, and carbonate ions. Organic complexes also may be present.

The ferrous oxidation state, less strong in its complexing properties than the ferric, forms few inorganic complexes. Ferrous hydroxide, $Fe(OH)_2$, is a stronger base than ferric hydroxide. The ionization products include $FeOH^+$ and Fe^{++}. Ferrous anions such as hypoferrite, FeO_2^{--}, form in strongly alkaline solutions. But, ferrous iron probably occurs most frequently in natural waters as the simple Fe^{++} ion.

Although the array of iron species is formidable, thermodynamic calculations show that those ions which predominate in dilute solutions under conditions which are commonly found in natural waters constitute a much smaller group. The pertinent thermodynamic data available for this purpose are given in tables 1 and 2.

TABLE 1.—*Equilibrium constants*

[Dissolved species indicated by (aq), solid phase by (c)]

Equilibrium	Equilibrium constant	Source of data
$Fe(OH)_2(aq) = FeOH^+ + OH^-$	2×10^{-5}	Computed.
$FeOH^+ = Fe^{++} + OH^-$	4.5×10^{-6}	Leussing and Kolthoff, 1953.
$Fe(OH)_2(c) = Fe^{++} + 2OH^-$	1.8×10^{-15}	Latimer, 1952.
$Fe(OH)_2(c) = FeOH^+ + OH^-$	4×10^{-10}	Leussing and Kolthoff, 1953.
$Fe(OH)_2(c) = FeO_2H^- + H^+$	5×10^{-19}	Schrager, 1929.
$Fe(OH)_3(aq) = Fe(OH)_2^+ + OH^-$	2.5×10^{-8}	Computed.
$Fe(OH)_2^+ = FeOH^{++} + OH^-$	4.5×10^{-10}	Latimer, 1952.
$FeOH^{++} = Fe^{+++} + OH^-$	2.7×10^{-12}	Do.
$Fe(OH)_3(c) = Fe^{+++} + 3OH^-$	6×10^{-38}	Elder, 1930; Latimer, 1952.
	1×10^{-38}	Jellinek and Gordon, 1924.
	3.2×10^{-36}	Evans and Pryor, 1949.
	1×10^{-42}	Pourbaix, 1949.
$Fe(OH)_3(c) = Fe(OH)_2^+ + OH^-$	5.3×10^{-17}	Latimer, 1952
$Fe(OH)_3(aq) = Fe^{+++} + 3OH^-$	4.0×10^{-29}	Do.
$Fe^{+++} + Cl^- = FeCl^{++}$	33	Do.
$FeCl_2^+ + Cl^- = FeCl_3(aq)$	.1	Do.

TABLE 2.—*Free energy data*

[Dissolved species indicated by (aq), solid phase by (c)]

Species	Free energy (kilocalories)	Source of data
Fe^{+++} (aq)	−2.53	Latimer, 1952
$FeOH^{++}$ (aq)	−55.91	Do.
$Fe(OH)_2^+$(aq)	−106.2	Do.
$Fe(OH)_3$(aq)	−154.4	Computed
$Fe(OH)_3$(c)	−166.0	Latimer, 1952
	−172.7	Pourbaix, 1949
FeO_4^{--}(aq)	−111.8	Do.
Fe_3O_4(c)	−241.8	Do.
Fe^{++}(aq)	−20.3	Do.
$FeOH^+$(aq)	−65.2	Leussing and Kolthoff, 1953
$Fe(OH)_2$(aq)	−109.6	Computed
$Fe(OH)_2$(c)	−115.6	Latimer, 1952
FeO_2H^-(aq)	−90.2	Pourbaix, 1949
$FeCl_3$(aq)	−97.1	Latimer, 1952
$FeCl_3$(c)	−80.4	Do.
$FeCl^{++}$(aq)	−35.9	Do.
$FeCl_2^+$ (aq)	−66.1	Do.

STABILITY-FIELD DIAGRAM

The intensity of oxidizing or reducing conditions in a solution is commonly represented by its "redox potential" (reduction-oxidation potential) or Eh. This value is expressed in volts compared to the normal hydrogen electrode, and in this paper the European sign convention is used (increasingly oxidizing conditions are represented by increasing positive values of Eh). Under conditions of chemical equilibrium in a solution containing ferric and ferrous iron, the redox potential is a function of the relative activities of the oxidized and reduced forms of iron that are present.

Again, under equilibrium conditions, the degree of dissociation of the ferric or ferrous hydroxide is a function of the hydrogen-ion concentration or pH of the solution.

A convenient means of representing these relationships is the stability-field diagram. This diagram is a plot of pH against Eh on which areas may be blocked out by thermodynamic computations to show under what conditions specific ionic species dominate. Figure 1 is a stability-field diagram for dilute solutions of iron, prepared from data in tables 1 and 2.

Calculations show that theoretically, in areas at the top and bottom of the diagram, water itself would be oxidized or reduced, respectively. Therefore, the possible conditions in water solution are in that part of the diagram where water is stable.

A value of 2×10^{-7} molal was selected arbitrarily for the total activity of iron in the system shown in the diagram. This value represents about 0.01 ppm, the lower limit of detection by methods commonly used in water analysis. It should be noted, however, that effective concentrations, or activities, are used in the diagram. These are some-

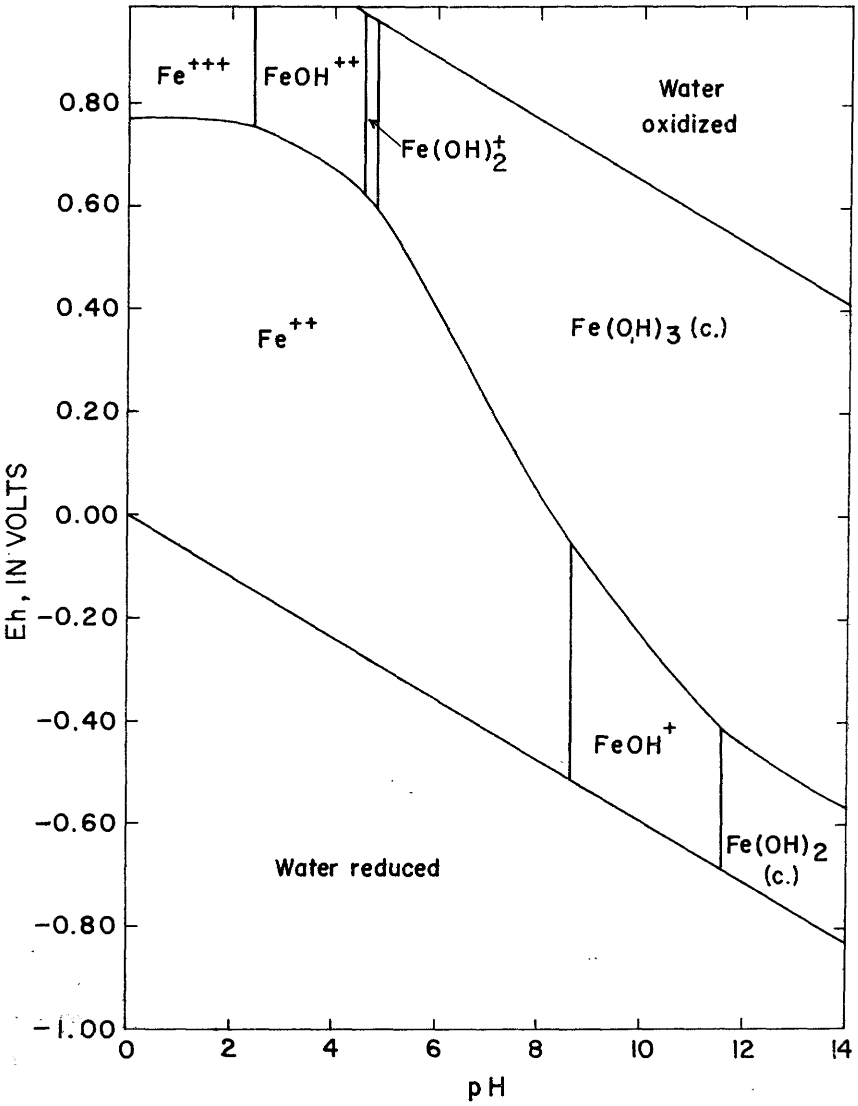

FIGURE 1.—Stability-field diagram for aqueous ferric-ferrous system.

what smaller than the actual concentrations that would be reported in chemical analyses, but the difference is minor in very dilute solutions.

The fundamental relationship which fixes the position of the line dividing oxidized from reduced species is the Nernst equation:

$$\mathrm{Eh} = E^\circ + \frac{RT}{nF} \, ln \, \frac{A \text{ ox.}}{A \text{ red.}}$$

where

Eh=redox potential
E°=standard oxidation potential; for
$Fe^{++} \longrightarrow Fe^{+++} + e = +0.771$ v
R=universal gas constant (1.987 calories/degree mole)
T=temperature in degrees Kelvin
n=number of electrons involved in chemical reaction
F=Faraday constant (96,484 absolute coulombs)
A ox.=activity of oxidized form of ions
A red.=activity of reduced form of ions

For the ferrous-ferric system at 25° C, the equation becomes

$$Eh = 0.771 + 0.0592 \log \frac{[Fe^{+++}]}{[Fe^{++}]}$$

The pH of the solution affects the activity of the ions involved, both through formation of hydroxide complexes and through precipitation of solid hydroxides.

The positions of lines on figure 1 representing boundaries between different ferric species are independent of Eh and were calculated from dissociation constants in table 1. For example, for

$$FeOH^{++} \rightleftharpoons Fe^{+++} + OH^-$$

the value of K is 2.7×10^{-12}. Hence

$$\frac{[Fe^{+++}][OH]}{[FeOH^{++}]} = 2.7 \times 10^{-12}$$

and when

$$\frac{[Fe^{+++}]}{[FeOH^{++}]}$$

has a value of unity (equal activities of each being present), the activity of OH^- will be 2.7×10^{-12}, and the pH of the solution is 2.4. A similar computation gives the position of the $FeOH^{++}-Fe(OH)_2^+$ boundary as pH 4.6. The $Fe(OH)_2^+-Fe(OH)_3(c)$ boundary is located from the equilibrium constant for

$$Fe(OH)_3(c) \rightleftharpoons Fe(OH)_2^+ + OH^-$$

assuming half the iron present, 1×10^{-7} moles per liter, is in the $Fe(OH)_2^+$ form. This computation gives a pH value of 4.8. The pH range over which the $Fe(OH)_2^+$ species predominates, therefore, is very narrow.

Similar computations based on data for ferrous species fix the Fe^{++}–$FeOH^+$ boundary at pH 8.7 and the $FeOH^+$–$Fe(OH)_2(c)$ boundary at pH 11.6.

The position of the line separating ferric and ferrous species was found by computing the Eh for unit values of pH from 0 to 14, using the Nernst equation. The activities of Fe^{+++} and Fe^{++} were computed for each value of pH. The maximum amount of either that can be present is 10^{-7} moles per liter. The contents of ferric and ferrous ions, however, are lowered by formation of hydroxides. The interplay of these effects, as the different hydroxides form at different pH levels, is represented in the diagram by a line whose slope changes as it passes each of the pH levels at which a change in dominant ferric or ferrous species occurs.

A general technique for computing the position of the ferrous–ferric boundary is indicated by the following computations. From pH 0 to about 1.0

$$[Fe^{+++}]=10^{-7}-[FeOH^{++}]$$

$$[FeOH^{++}]=\frac{[Fe^{+++}][OH^{-}]}{2.7\times10^{-12}}$$

Combining these equations and substituting a value for $[OH^{-}]$ computed from the assumed pH, the value of $[Fe^{+++}]$ may be computed. At pH 0, the computed value is 0.99×10^{-7} for $[Fe^{+++}]$. Similar computations are required to give the value of $[Fe^{++}]$. However, at pH values below about 7.0, the amount of the $FeOH^{+}$ form is negligibly small. At pH 0, we may obtain the value of Eh from the Nernst equation

$$Eh=E^{\circ}+0.0592\log\frac{0.99\times10^{-7}}{1.0\times10^{-7}}$$

For all practical purposes, Eh at this pH is equal to E°, or 0.771 volts.

At higher pH levels, the less completely dissociated hydroxides also must be taken into account where appropriate. At pH 4, for example, the $[Fe^{+++}]$ value is affected by both the dissociation reactions

$$Fe(OH)_2^{+}\rightleftharpoons FeOH^{++}+OH^{-}$$

and

$$FeOH^{+}\rightleftharpoons Fe^{+++}+OH^{-}$$

In the range above pH 5, however, the corrections for other ionic forms of ferric iron are minor compared to the effect of the low solubility of ferric hydroxide. The values for $[Fe^{+++}]$ in that range can be computed directly from the solubility product, here taken as 6×10^{-38} (Latimer, 1952).

An alternate and perhaps simpler method for computing the position of the ferrous-ferric boundary suggested by R. M. Garrels (written communication) and similar to that of Pourbaix (1949) uses the standard potentials for the redox couples which predominate at the various pH levels. For example, between pH 2.4 and 4.6, the predominant ferric form is $FeOH^{++}$ and the predominant ferrous form is Fe^{++}. The couple involving these ions is

$$Fe^{++}+OH^{-}\rightleftharpoons FeOH^{++}+e$$

The standard free energy change ΔF° for this reaction can be computed from free energy values given in table 2, subtracting the total free energy of reactants from that of the product, and is equal to +1.99 kilocalories. The standard potential, E°, for the reaction can be computed from the free energy change by means of the relation

$$E^\circ=\frac{\Delta F^\circ}{n\times 23.06}$$

where n is the number of electrons shown in the couple as written. The standard potential for the reaction here has a value of +.086 volt. The Eh for any point on the ferrous-ferric boundary between pH 2.4 and 4.6 can now be computed from the Nernst equation which takes the form

$$Eh=0.086+0.0592\log\frac{[FeOH^{++}]}{[Fe^{++}][OH^{-}]}$$

or, because ferrous and ferric contents are equal at the boundary,

$$Eh=0.086+0.0592\ (14-pH)$$

At very high pH, anionic forms of iron may exist, but that possibility was not taken into account in preparing figure 1 because such pH values are not attained in natural waters.

The stability-field diagram helps to summarize the theoretical aspects of the chemistry of iron in dilute solutions. Departures from behavior predicted on theoretical grounds may occur in natural waters. Some of these deviations result from the chemical instability of waters removed from their original environments. Other factors not considered in the diagram include formation of other types of complex ions and the existence of colloids or suspensions of solid-phase iron.

POSSIBLE EXISTENCE OF $Fe(OH)_3$ AQUEOUS AND $Fe(OH)_2$ AQUEOUS

Detectable amounts of iron occur in many natural waters whose pH and Eh plot in the $Fe(OH)_3$ (c) field in figure 1, although theoretical considerations indicate that the amount in solution should be far below the limits of detection by standard procedures. Some of the iron in these waters could be present as dissolved undissociated hydroxide. $Fe(OH)_3$ (aq) and $Fe(OH)_2$ (aq) are not specifically mentioned in most of the published literature, but some experimental data do exist from which computations can be made to indicate the possible importance of these two forms of iron.

The work of Lamb and Jacques (1938) on the hydrolysis of ferric chloride in dilute solutions indicates that solutions containing ferric hydroxide generally are supersaturated. They showed that the rate at which $Fe(OH)_3$ was precipitated from such solutions decreased as the concentration decreased, reaching zero at a concentration of 2×10^{-9} molar. They give this value as the solubility of ferric hydroxide in undissociated form (p. 1220), $Fe(OH)_3$ (aq). A value for *K* for the equilibrium

$$Fe(OH)_3(aq) \rightleftarrows Fe(OH)_2^+ + OH^-$$

can be computed from this value for total solubility, assuming a neutral pH and amounts to 2.5×10^{-8}.

Oka (1940) gives 1.3×10^{-5} molar as the total solubility of ferrous hydroxide in pure water, and Schrager (1929) gives 3.5×10^{-5} molar as the solubility in a solution 1.375 N in OH^-. The amounts of Fe^{++} and $Fe\ OH^+$ present at high pH, computed from equilibrium constants in table 1, are substantially less than these solubilities, which suggests the possible presence of $Fe(OH)_2$ (aq). A value for *K* for the equilibrium

$$Fe(OH)_2\ (aq). \rightleftarrows FeOH^+ + OH^-$$

estimated from these data, is about 2×10^{-5}.

The thermodynamic properties of the dissolved molecular species differ from those of the solid-phase material, and if the existence of $Fe(OH)_3$ (aq) and $Fe(OH)_2$ (aq) had been assumed in the preparation of figure 1, the position of some of the lines would have been somewhat different. The most marked differences would occur at high pH. Data used in preparing figure 1 were taken from Latimer (1952). The existence of dissolved, undissociated species was not assumed.

More experimental work would be required to establish the prevalence of undissociated dissolved species in natural water. Their practical significance, in any event, is not great because the dissolved $Fe(OH)_3$ (aq)would be below the limits of detection by ordinary means, and the ferrous species could exist only at pH levels far above those of natural water.

An explanation of the phenomena reported by Lamb and Jacques (1938) might be that stable colloidal or subcolloidal systems of $Fe(OH)_3$ are found. The existence of such systems in natural water is described on page 25.

MAXIMUM SOLUBILITY OF IRON

The maximum activity of iron that can be present in solution is a function of Eh and pH, and the form of the dissolved iron also is a function of those properties. The theoretical relative proportions of the various forms of iron can be calculated for any pH or Eh, and the maximum activities of iron that could be present can then be computed. Figure 2 represents the results of such computations for Eh values of +0.50, +0.40, +0.30, +0.20, +0.10, 0, and −0.10 volts.

In preparing the diagram, the proportion of $[Fe^{+++}]$ to $[Fe^{++}]$ was computed for each Eh by substituting that value for Eh in the Nernst equation. Over most of the pH–Eh range, the ferric species are only very slightly soluble. Values for $[Fe^{+++}]$ were computed for two or more pH values for each Eh, using solubility product and dissociation constants, as was done in preparing figure 1. The $[Fe^{+++}]$ value being known, the $[Fe^{++}]$ value was computed from the Nernst equation relationship for that Eh. The dissociation constant was then used to compute $[FeOH^{+}]$. The sum of the amounts of all forms is the total activity of iron.

In most of the area of the diagram, the lines for the different Eh values have a steep, negative slope and are essentially parallel. This expresses the rapid decrease in solubility of ferric iron with increasing pH, and through much of the pH range, the solubility product of $Fe(OH)_3$ is the dominant factor in the solubility calculation. The slope of the lines for $Eh=0$ and -0.10 decreases slightly at higher pH values because of the presence of some $FeOH^{+}$. At low pH, the slope of the 0.50 Eh line also decreases because of the formation of ferric hydroxide complexes.

The solubilities given by figure 2 are activities and are less than actual concentrations. Techniques for computing activity from concentration values are given in another report.[1]

OCCURRENCE OF FERROUS IRON IN NATURAL WATERS

The area bounded by pH 5.0 and 8.0 and by Eh 0.3 and 0.5 on figure 1 includes most of the range that has been observed in natural waters exposed to the atmosphere. About two thirds of this area lies in the ferric part of the field, and only in waters that plot in the remaining one third of the area should there be detectable amounts of iron in solution. If waters plotted in this area are high in iron, most of it should be in the ferrous state. By extrapolation of figure 2, a maximum of somewhat more than 100 ppm of ferrous iron could be present at Eh 0.3 and pH 5.0.

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[1] Hem, J. D., Chemistry of iron in natural water—Restraints on dissolved ferrous iron imposed by bicarbonate, redox potential, and pH: U.S. Geol. Survey Water-Supply Paper 1459–B in preparation.

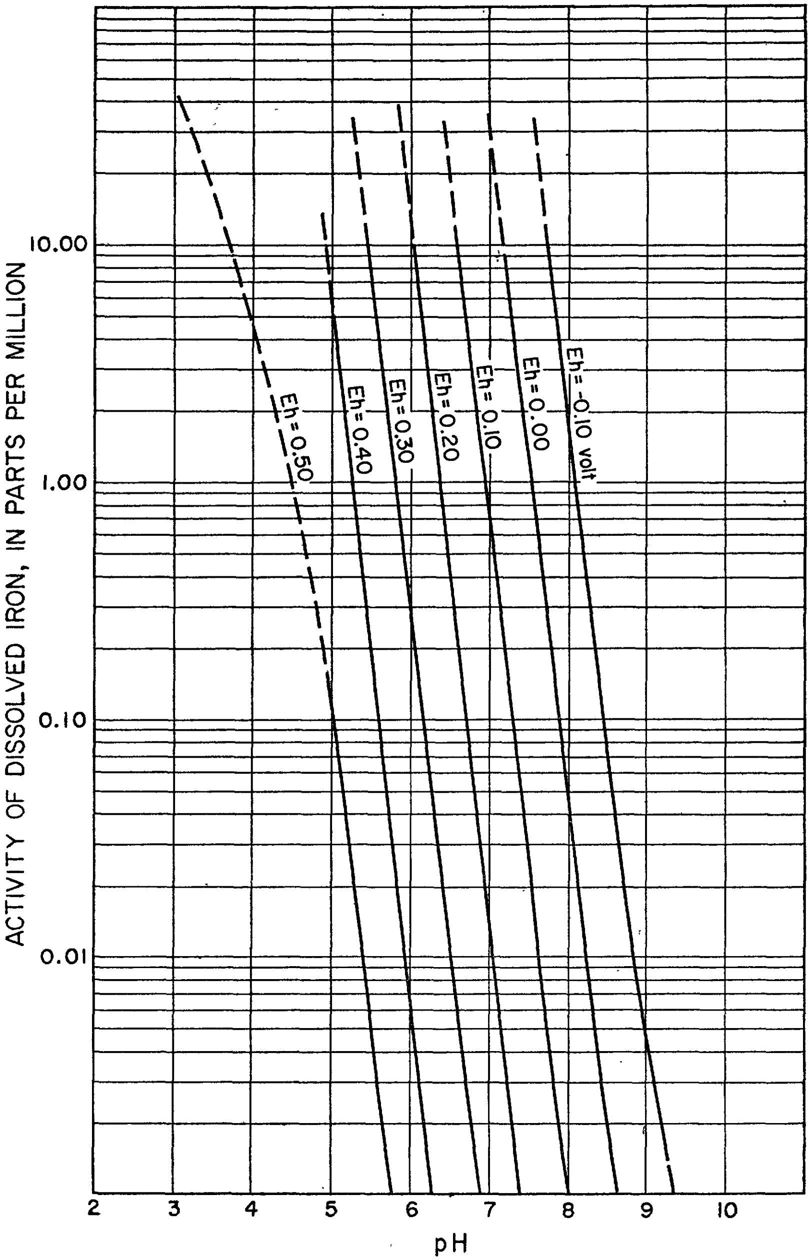

FIGURE 2.—Relation of total activity of iron in water to pH and Eh.

Waters that are high in iron generally contain it in the ferrous form. However, dissolved ferrous iron would be oxidized to the ferric state by atmospheric oxygen under the pH–Eh conditions that are ordinary in natural waters near the surface of the ground. At low pH, the reaction is slow. It has been investigated in a low pH range by Lamb and Elder (1931). Oxidation half-lives for the reaction at various pH's are listed as follows:

pH	Half life (days) Initial (Fe^{++}) = ±0.15 molal
−0.48	105
.00	83
.30	85
.64	86
1.36	69
1.92	43
2.1	22

At pH's much above 2.1, ferric hydroxide begins to precipitate, and the kinetic situation becomes considerably more complicated. The reaction has not been investigated elsewhere for the pH range of present interest (approximately 5–8), but qualitative data have been obtained in this investigation.

EXPERIMENTS WITH SOLUTIONS OF FERRIC AND FERROUS IRON

Five solutions were made up with distilled water and various proportions of ferric and ferrous chloride, and the pH, Eh, and iron concentrations in the solutions were measured at intervals for about a week. The results of these measurements are given in table 3.

The solutions having an initial pH of 3.4 (solutions 2, 3, and 5) had a relatively high initial Eh, and were the three solutions whose initial ratio

$$\frac{\text{ppm Fe}^{+++}}{\text{ppm Fe}^{++}}$$

was 1.0 or higher. The value determined for Eh decreased with time for all three solutions.

Solutions 1 and 4 contained more ferrous iron than ferric and had higher initial pH's and lower Eh's than the other three. In these two solutions, the Eh increased with time.

Considerably more Fe^{+++} was added to each solution than could be retained at the pH that existed in the solution. The observed changes in Eh represent an approach to equilibrium in the solutions exposed to air. The ferrous iron content did not change much in any of the solutions except No. 5; hence, most of the adjustment to reach equilibrium in the Fe^{+++}/Fe^{++} relationship must have occurred in the

TABLE 3.—*Eh, pH, and ferrous ion concentration measurements on prepared solutions*

Initial iron concentration	Time (hours)	Ferrous ion concentration (ppm)	pH	Measured Eh (volts)
Solution 1 ± 12 ppm Fe^{++} ± 2 ppm Fe^{+++}	0.7	10.8	4.5	0.453
	2.2	11.0	4.5	.463
	5.2	10.1	4.5	.474
	26.0	11.9	4.5	.491
	53.9	10.6	4.4	.503
	145	10.8	4.3	.503
Solution 2 ± 12 ppm Fe^{++} ± 12 ppm Fe^{+++}	4.7	13.8	3.4	0.638
	6.8	13.8	3.4	.627
	24.0	13.5	3.4	.610
	47.8	13.8	3.4	.604
	126.2	13.8	3.4	.597
	145	13.8	3.4	.598
Solution 3 ± 2 ppm Fe^{++} ± 12 ppm Fe^{+++}	4.7	1.23	3.4	0.691
	6.8	1.22	3.4	.687
	24.0	1.20	----------	.672
	47.8	----------	----------	.663
	126.2	----------	----------	.651
Solution 4 ± 12 ppm Fe^{++} ± 0.2 ppm Fe^{+++}	1.0	11.9	5.0	0.425
	2.7	11.4	5.0	.434
	4.9	11.9	5.0	.443
	26.6	11.0	4.8	.461
	119	10.5	4.4	.497
Solution 5 ± 0.2 ppm Fe^{++} ± 12 ppm Fe^{+++}	1.0	0.29	3.4	0.741
	2.7	.28	3.4	.732
	4.9	.23	3.4	.723
	26.6	.18	3.5	.699
	119	----------	3.4	.681

ferric form. This instability of ferric iron is indicated also by the fact that all the solutions except No. 5 plot in the Fe^{++} field in figure 1.

Measured Eh and pH values for these solutions, when plotted in figure 2, do not coincide with the iron concentrations added to the solutions when they were made up. This fact and the changing Eh also suggest nonequilibrium conditions.

Another factor that affected these solutions was the rate of oxygen diffusion through the solution, and a source of some uncertainty is the fact that the oxygen couple is not reversible. As a result, true Eh values of this couple are hard to measure.

The behavior of iron in natural ground waters has some similarity to that in solutions 1 and 4. Natural waters tend to have a low Eh that rises to a value near 0.50 v in samples that are removed from the source and stored for a time in contact with air.

USE OF Eh AND pH MEASUREMENTS TO EVALUATE IRON SYSTEMS

The iron in samples of iron-bearing ground waters is generally not in equilibrium. Ferric hydroxide precipitation has not reached the level predicted by the solubility product, and the reaction between the ferrous ion and oxygen has not had sufficient time to establish constant ferric and ferrous ion concentrations. Very likely, all other important reactions are essentially in equilibrium.

One approach to a system which is not entirely in equilibrium, is to use the Nernst equation and Eh measurements. The validity of these calculations, however, cannot be taken for granted. In the first place, it may not be certain that reversible conditions are present at the electrode. Secondly, activity coefficient corrections may be important. Several experiments have been made to show, as quantitatively as possible, that theoretical calculations check the results from Eh-Nernst equation calculations.

One method used was similar to that described by Lamb and Elder (1931). Measured quantities of a solution of standard potassium permanganate were added to acidified solutions containing $FeCl_2$ and $FeCl_3$. The change in concentration of ferrous ion was calculated from the permanganate volume; this was then checked against a calculation for the same quantity using the Nernst equation. The results of the calculations are given in table 4. The agreement is as good as can be expected considering the inaccuracies in the Eh readings and in the determination of iron, and the way in which the inaccuracies are magnified by the calculations. These results show that Eh readings will follow accurately the change in concentration of Fe^{++} during its oxidation in acid solution.

Another experiment was made for a similar purpose at higher pH's. A good theoretical check is more difficult under these conditions, and significant results were not obtained above pH 4.1. The procedure was to calculate the concentration of ferric ion, first from Eh data and measured values for the ferrous-ion concentration. This was done by means of the Nernst equation. Then the quantity was calculated by an independent method, using measured values for the pH and the total concentration of ferric species. Results are given in table 5. Considering the uncertainties in the ionization constants and the analytical data, the agreement between $[Fe^{+++}]$ values from the two calculations is reasonable. It is interesting to note that $[Fe^{+++}]$, calculated by these methods, is consistently higher than that calculated from the solubility expression

$$[Fe^{+++}]\ [OH^-]^3 = 6 \times 10^{-38}$$

Close agreement is not to be expected because of the various ionic species present, and also because equilibrium probably had not been reached in the $Fe(OH)_3$ precipitation reaction. It might be noted also that the above calculations assume that the two reactions involved in hydrolysis

$$Fe^{+++} + OH^- \rightleftharpoons FeOH^{++}$$

$$FeOH^{++} + OH^- \rightleftharpoons Fe(OH)_2^+$$

have reached equilibrium. The success of these calculations is further evidence that the hydrolyses are rapid and reach equilibrium quickly.

TABLE 4.—*Nernst equation and theoretical calculations of ferrous ion oxidized by potassium permanganate* [1]

Volume $KMnO_4$ added 0.0004970 N (milliliters)	Δ *E* uncorrected (millivolts)	Δ *E* corrected (millivolts)	Δ *C* calculated from Nernst equation (ppm)	Δ *C* calculated from volume of $KMnO_4$ (ppm)
Solution 1 [2]				
0.01	0	0	0	0
2.00	7	7	0.6	1.2
4.00	19	18	1.8	2.3
6.00	30	29	3.1	3.5
8.00	41	39	4.4	4.6
10.00	48	44	5.1	5.7
12.00	59	54	6.4	6.8
14.00	66	61	7.2	7.9
16.00	78	72	8.8	9.0
18.00	90	84	9.2	10.1
Solution 2 [3]				
0.00	0	0	0	0
2.00	5	5	2.8	1.1
4.00	7	6	3.5	2.2
6.00	11	9	5.3	3.3
8.00	12	9	5.3	4.5
10.00	15	10	5.8	5.6
15.00	21	15	9.0	8.3
20.00	27	20	12.2	11.2
25.00	32	22	13.6	14.0
30.00	37	26	16.2	16.8
35.00	41	29	18.2	19.5
Solution 3 [4]				
0.00	0	0	0	0
2.00	2	2	1.5	1.1
4.00	5	4	2.6	2.2
6.00	8	6	3.9	3.3
8.00	10	7	4.6	4.5
10.00	13	8	5.3	5.6
12.00	16	11	7.4	6.7
14.00	17	11	7.4	7.8
16.00	19	13	8.7	8.9
21.00	26	20	13.4	11.7
26.00	31	21	14.1	14.5
31.00	37	26	17.4	17.3

[1] Various acidified solutions of $FeCl_2$—$FeCl_3$ were oxidized with measured quantities of standard $KMnO_4$ solution. Calculations were made in two ways for the amount of Fe^{++} oxidized per liter (Δ*C*): First, using the Nernst equation and measured changes in the Eh (Δ*E*); second, using the volume of the $KMnO_4$ and its normality (0.0004970). Δ *E* correction after Lamb and Elder (1931).

[2] Characteristics of solution 1:

Fe^{++} = 11.25 ppm
Fe^{+++} = 2.50 ppm
pH = 1.6
Original volume before addition of $KMnO_4$ = 50.00 ml

[3] Characteristics of solution 2:

Fe^{++} = 48.5 ppm
Fe^{+++} = 19.5 ppm
pH = 1.6
Original volume of solution = 50.00 ml

[4] Characteristics of solution 3:

Fe^{++} = 43.5 ppm
Fe^{+++} = 26.8 ppm
pH = 1.6
Original volume of solution = 50.00 ml

Table 5.—*Ferric ion concentrations calculated by two independent methods*

Total Fe^{+++} concentration (ppm)	pH	Fe^{++} concentration (ppm)	Eh (volts)	$[Fe^{+++}]$ calculated from total ferric concentration and pH (molal)	$[Fe^{+++}]$ calculated from ferrous concentration and Eh (molal)	$[Fe^{+++}]$ calculated from solubility product (molal)
6.1	3.6	2.5	0.707	3.0×10^{-6}	3.2×10^{-6}	1.2×10^{-7}
6.1	3.6	9.8	.668	2.7×10^{-6}	3.2×10^{-6}	1.2×10^{-7}
1.7	4.1	10.6	.590	1.0×10^{-7}	1.6×10^{-7}	5.9×10^{-9}
1.4	4.1	42.5	.535	$3\ \times10^{-8}$	$8\ \times10^{-8}$	5.9×10^{-9}

No method was found for investigating nonequilibrium iron systems at higher pH's. Huber and Garrels (1953) have taken Eh and pH data in $FeCl_2$ solutions under a wide variety of conditions. In their experiments, $[Fe^{++}]$ was high enough to produce equilibrium rather quickly. They found good agreement between results from the Nernst equation and from equilibrium calculations.

The experiments that have been described and the interpretation of results, seem to show that the Nernst equation is effective for defining an iron system in a natural water provided that certain rather restrictive conditions are met. The system must be stable under the conditions in which the properties of the water are being measured, so that the iron system will be in equilibrium; complicating factors, including complexing or chelation and deviations from assumed activity coefficients, must be insignificant or known. To be measured accurately, the Eh must be set by a reversible electrode system. Many natural waters do not fit these conditions. However, the Nernst equation may be useful for estimating the Eh of ground waters in their natural environments where that property cannot be directly measured. This use will be discussed later in this report.

ORIGIN OF FERROUS IRON IN WATER

Using the assumptions developed, a qualitative explanation can be formulated for the origin of ferrous iron in wells and springs. Water below the land surface and not in contact with air probably has Eh values of 0.20 volts or less and a relatively low pH (less than 6) if enough excess carbon dioxide is present. Under these conditions, ferrous solutions as high in iron as 50 ppm are permanently stable. As the water approaches the surface of the ground and dissolves oxygen from the air, the nonequilibrium situation described above sets in. Water low in Eh and high in Fe^{++} is continually supplied. Ferrous-ion oxygenation and ferric-hydroxide precipitation both continue. If the low-Eh water is supplied rapidly enough, the level of the ferrous-ion concentration will remain high, even though the

Eh at the surface may be considerably above what equilibrium calculations indicate is compatible with the presence of dissolved ferrous ion.

COMPUTATION OF Eh IN GROUND-WATER AQUIFERS

Granite Spring in the foothills of the Front Range a few miles west of Boulder, Colo., discharges natural ferrous-iron bearing water. The spring issues from a fissure in granite and forms a small pool enclosed by a wooden shelter. The water is high in bicarbonate, sulfate, and sodium (see table 6) and also contains about 16 ppm of iron The measured pH and Eh of water in the spring pool were 6.3 and 0.34 volts, respectively, at a temperature of 19° C. The flow of the spring is about a gallon a minute, or less, and the water was very clear. Samples were obtained in two 1-gallon Pyrex bottles and several 4-ounce polyethylene bottles, all of which were tightly stoppered. One of the 1-gallon samples was acidified with hydrochloric acid to a pH of about 1.5. The 4-ounce samples were not acidified. All the samples were allowed to stand stoppered in the laboratory; and the concentration of ferrous iron, the Eh, and the pH were measured from time to time. Results of the tests on the untreated samples only are given in table 7.

The acidified sample retained all the original ferrous iron after 90 days of storage. The untreated samples became noticeably turbid

Table 6.—*Chemical analysis, Granite Spring near Boulder, Colo.*[1]

[Parts per million except as indicated]

Constituent	July 27, 1956	
	ppm	epm
Silica (SiO_2)	62	-------
Iron (Fe)	16	-------
Manganese (Mn)	.45	-------
Calcium (Ca)	536	26.75
Magnesium (Mg)	97	7.98
Sodium (Na)	1,580	68.73
Potassium (K)	51	1.30
Bicarbonate (HCO_3)	2,010	32.94
Carbonate (CO_3)	0	.00
Sulfate (SO_4)	2,220	46.22
Chloride (Cl)	880	24.82
Fluoride (F)	2.0	.11
Nitrate (NO_3)	.4	.01
Phosphate (PO_4)	.00	-------
Dissolved solids:		
Calculated	6,420	-------
Residue on evaporation at 180° C	6,410	-------
Hardness as $CaCO_3$	1,740	-------
Noncarbonate hardness as $CaCO_3$	90	-------
Specific conductance (micromhos at 25°C)	8,190	-------
pH	6.5	-------
Color	5	-------
Percent sodium	66	-------

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[1] Source: spring pool at enclosure; location: Boulder County, Colo. (5 mi. NE of Boulder); discharge: One-half gpm flow (est.); temp: 60° F; appearance: very slight opalescence; Water-bearing formation: igneous-granite; owner: Mrs. M. L. Champion, 7860 W. Colfax, Denver, Colo. Remarks: Few gas bubbles in pool.

overnight and in a few days had a considerable precipitate of red ferric hydroxide.

Do the field data on pH and Eh represent water of Granite Spring as it existed underground? Figure 1 indicates that these values of pH and Eh intersect at the edge of the Fe^{++} area, but figure 2 shows that the solubility of iron under these conditions is only about 0.01 ppm. The ferrous iron in the water, therefore, is unstable. Presumably, the underground conditions in which the water occurred favored retention of all the iron in solution in ferrous form without instability. The water is strongly buffered by the presence of carbon dioxide and HCO_3^-; consequently, the pH of 6.3 measured in the spring pool probably is essentially the same as the water had before it reached the land surface. The measured Eh probably represents non-equilibrium conditions. However, the Eh of this water before it reached the land surface can be computed by means of the Nernst equation. To do this, all the iron is assumed to be present as Fe^{++}, and the amount of Fe^{+++} is computed from the pH. This computation gives an Eh value of about 0.14. About the same result can be obtained from figure 2, where the intersection of pH 6.3 and 16 ppm of iron gives an Eh value midway between 0.10 and 0.20 v. A more refined calculation requires use of activities rather than concentrations of iron and would give a result nearer 0.20 volts.

The studies of Granite Spring suggest that the Eh of a ground water measured in the field does not necessarily represent conditions at depth in the ground-water body. However, if certain assumptions are made, the Eh in the underground environment can be estimated from the pH determined in the field, and from the iron content of the water determined in the latoratory. This procedure avoids the difficult task of measuring Eh in aquifers.

Assumptions required in computing Eh are:

1. That chemical equilibrium exists in the aquifer so far as oxidizing and reducing conditions and solution and deposition of iron are concerned.
2. That the aquifer contains an excess of solid-phase iron available for solution.
3. That complexing by organic or other materials is absent or negligible.
4. That pH is maintained by a buffer system so that it does not change appreciably when the water leaves the aquifer, and that the sample represents the iron content of the water in the aquifer. Whether all iron remains in solution until the sample is analyzed is immaterial, however.

The water should be relatively dilute. Activity corrections can be applied to waters of moderately high dissolved solids, but the procedure is not applicable to brines.

Many ground waters come reasonably close to fulfilling the assumed conditions. If the iron content is less than about 0.25 ppm, however, the accuracy of the determination may be low, and the validity of assumption 2 (above) is questionable.

TABLE 7.—*The stability of waters containing ferrous iron*

Time (days)	Ferrous concentration (ppm)	pH	Eh (volts)
Granite Spring sample [1]			
0	14.5	6.3	0.34
1.0	7.5		
2.0	3.8		
6.0	1.4		
7.0	.7		
9.0	.2	6.7	.42
12.0	.0		
Prepared sample: Solution 1 [2]			
0.0	16.9	6.5	0.16
3.0	11.4	6.5	.18
5.5	11.6	6.5	.20
24.0	9.3	6.5	.20
30.0	8.1	6.7	.20
94.5	.0	6.7	.20
Prepared sample: Solution 2 [3]			
0.1	7.7	6.8	0.17
3.7	.0	6.9	.20
23.8	.0	6.9	.32
Solution 3 [4]			
0.0	26.2	6.2	0.28
1.9	14.4	6.3	.31
3.9	1.5	6.6	.32
6.9	.0	6.6	.39
Solution 5 [5]			
0.0	13.8	6.4	0.24
1.9	1.1	6.6	.27
4.8	.0	7.0	.41
Solution 6 [6]			
0.1	17.9	5.8	0.30
2.8	14.4	5.6	.43
3.8	13.1	5.8	.30
4.8	11.9	5.8	.40
5.8	9.5	5.8	.43
6.8	8.5	5.8	.52
11.8	4.4	5.7	.46
20.8	2.0	5.6	.56
29.0	1.1	5.4	.52
Solution 7 [7]			
0.0	16.0	6.4	0.32
2.8	6.5	6.4	.39
3.8	2.9	6.4	.26
4.7	.95	6.4	.37
5.7	.04	6.6	.54
Solution 8 [8]			
0.0	17.9	6.2	0.35
1.0	12.5	6.4	.30
1.8	9.1	6.2	.35
2.8	4.6	6.3	.44
3.8	2.0	6.5	.43
8.8	.0	6.6	.48
Solution 9 [9]			
0.2	14.4	6.3	0.28
.9	9.5	6.3	.33
1.9	4.9	6.3	.36
6.9	.3	6.4	.51
Solution 10 [10]			
0.25	11.8	6.7	0.45
.50	9.0	6.5	.37
21.5	.22	6.2	.51

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[1] Granite Spring sample (Denver Lab. No. 1690; collected 10/17/56; temperature of water at source, 19° C; allowed to stand with very little mixing or agitation):
(HCO_3^-)=1,990 ppm; $(SO_4^=)$=2,210 ppm; specific conductance=8,170 µmhos

[2] Solution 1, prepared sample; allowed to stand with a minimum of mixing and agitation:
(HCO_3^-)=1,490 ppm; $(SO_4^=)$=0.0 ppm

[3] Solution 2, prepared sample; identical with Solution 1 except that frequent mixing and agitation was effected.

[4] Solution 3; little mixing:
(HCO_3^-)=1,680 ppm; $(SO_4^=)$=±2,000 ppm

[5] Solution 5; little mixing:
(HCO_3^-)=2,000 ppm; $(SO_4^=)$=±2,000 ppm

[6] Solution 6; little mixing:
(HCO_3^-)=23 ppm; $(SO_4^=)$=±50 ppm; specific conductance: 543 µmhos

[7] Solution 7:
(HCO_3^-)=1,830 ppm; $(SO_4^=)$=±2,000 ppm; specific conductance: 6,400 µmhos

[8] Solution 8:
(HCO_3^-)=1,860 ppm; $(SO_4^=)$=±2,000 ppm; specific conductance: 6,670 µmhos

[9] Solution 9:
(HCO_3^-)=1,880 ppm; $(SO_4^=)$=0.0 ppm

[10] Solution 10: Identical to solution 6 except that initial pH is lower.

The Eh can be estimated from figure 2 by noting the position of the intercept of pH and total iron content with respect to the Eh lines, or the Eh can be computed from the Nernst equation. If this procedure were used, all the iron present could be assumed to be ferrous, unless the pH were very low. The ferric-ion concentration could be computed from the pH. For the most accurate results, activity corrections should be applied to the iron-concentration data. Temperature and pressure effects and other sources of error besides departures from the assumed conditions may affect Eh computations sometimes. Unconfined ground waters may decrease in Eh with depth below the top of the zone of saturation, especially if water levels fluctuate, so a sample may not represent conditions in the whole aquifer. More field experience is needed to see if the proposed procedure gives consistent results.

EXPERIMENTS WITH SYNTHETIC WATER SAMPLES

Some factors that affect the stability of ferrous iron in solution were studied by experiments with synthetic samples. Samples of distilled water were boiled for 30 minutes to expel dissolved oxygen, and various amounts of ferrous iron, bicarbonate, sulfate, and chloride were added. After a solution was prepared, it was placed in a stoppered bottle, but no attempt was made to exclude air during further work with the sample. The samples, with one exception, were not stirred or agitated.

The rate of oxidation should depend mainly on the rate at which oxygen from the air diffuses through the solution. Although the conditions of the experiment precluded accurate measurement of reaction rates or comparisons among samples, increasing the amount of mixing and thus of aeration speeded up the rate of reaction. This fact is shown by results for solutions 1 and 2 in table 7.

The concentrations of various anions do not seem to affect the stability of ferrous ions significantly. Bicarbonate, however, does affect observed changes in pH. The oxidation of ferrous iron produces ferric iron, which hydrolizes in three steps, liberating H^+, and finally precipitates as the hydroxide

$$Fe^{+++} + H_2O \rightleftharpoons H^+ + Fe(OH)^{++} + H_2O \rightleftharpoons Fe(OH)_2{}^+ +$$

$$H^+ + H_2O \rightleftharpoons Fe(OH)_3 + H^+$$

These H^+ ions react with HCO_3^- in the solution to give water and carbon dioxide.

$$H^+ + HCO_3^- \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2$$

These equilibria that involve carbonate also control the pH in most natural waters; and H^+ liberated in such a water, as in the hydrolysis of Fe^{+++}, becomes involved in the equilibrium reaction above. If the amount of H^+ is rather large compared to other components of the system, the pH may be considerably lowered and, in extreme cases, all the HCO_3^- may be removed from solution. Where the water contains much bicarbonate, the amount of H^+ needed to change the pH is considerably greater.

In several of the solutions listed in table 7, and in the water from Granite Springs, an analysis of which is also listed in table 7, nearly 2,000 ppm of bicarbonate was present initially. In order to maintain this concentration, the water must be exposed either to an atmosphere containing a higher percentage of carbon dioxide than the air, or must be under greater than atmospheric pressure, or is subject to both conditions. Therefore, when these waters were exposed to the air, they were unstable and lost carbon dioxide by evolution to the atmosphere. The loss of carbon dioxide causes the equilibrium to shift to the right and the H^+ concentration to decrease (raise the pH). Solutions 1–3, 5, and 7–9 all increased in pH while they were being studied as a result of the above effect, and this increase more than offset the tendency for the pH to decrease owing to Fe^{+++} hydrolysis reactions.

Although initial pH and Eh values for most of these solutions plot in the Fe^{++} area of figure 1, the iron systems would not be stable when exposed to air. Water exposed to the air would normally reach a stable Eh level of about 0.50 volts, owing to solution of oxygen. At this Eh, the amount of ferrous iron that could be present in equilibrium would be less than 0.01 ppm, unless the pH is below about 5.4.

The two most stable solutions studied were 1 and 6. Each retained considerable ferrous iron after 30 days. The slowness of oxidation of ferrous iron probably results from different characteristics of these solutions. Solution 1 had a low initial Eh and contained considerable bicarbonate and carbon dioxide. Solution 6 was low in dissolved solids and low in initial pH. Both plot farther from the Fe^{++}–$Fe(OH)_3$ boundary in figure 1 than the other solutions. One would expect ferrous iron to be oxidized more rapidly in those environments where pH and Eh values were nearer the $Fe(OH)_3$ area, and the behavior of the solutions is in general agreement with this anticipation.

Another factor which probably is involved in stabilizing solution 1 is the presence of excess carbon dioxide in solution. Evolved carbon dioxide probably formed a layer of impure carbon dioxide at the air-water interface which inhibited entry of oxygen in the solution. This effect would be eliminated by agitation of the water, as was shown by results with solution 2.

Another factor that tends to stabilize ferrous iron in solution 6 was the decrease in pH that occurred on standing. If the pH and Eh both increase with time, and they did in all solutions except 6 and 10, the ferrous iron should be increasingly unstable with the passage of time; at any rate, the changing conditions would encourage the reaction to go to completion. In solution 6, however, the increasing concentration of H^+ as the reaction proceeded tended to decrease the stability of ferric hydroxide. The pH and Eh of solution 10 were high enough to plot in the $Fe(OH)_3$ area of figure 1.

EFFECTS OF OTHER DISSOLVED CONSTITUENTS ON FERROUS IRON

The availability of oxygen in natural water is an important factor controlling the occurrence of dissolved iron. Ground waters and some types of surface-water bodies have limited access to air for a supply of dissolved oxygen. At appreciable distances below the surface in some surface-water bodies, the amount of oxygen in solution is below saturation. This condition is especially likely where oxidizing reactions, such as the ferrous-ion oxygenation reaction occur at depth, and in reducing environments such as decaying organic sediment.

Data from Hutchinson and others (1938) showing differences at depth in lakes are quoted in table 8. Dissolved iron (presumably in the ferrous state) increases and Eh decreases as the dissolved oxygen decreases. These tendencies are in agreement with the preceding discussion.

TABLE 8.—*Eh and iron concentrations measured at various depths in lakes*

[First set of data taken from Linsley Pond, North Brandford, Conn. on September 16, 1938; second set taken from Jobs Pond, Conn. on October 4, 1938. Source Hutchinson and others (1938)]

Depth (meters)	Temp. (° C)	Dissolved oxygen concentration (ppm)	Ferrous iron concentration (ppm)	Eh (volts)
First set of data				
0	20	8.0	0.0	0.47
2	20	7.8	.0	.47
5	15.2	4.0	.0	.50
7	9.5	1.0	1.4	.38
9	8.5	1.0	2.5	.30
11	8.0	.8	4.0	.20
13	7.8	.5	5.0	.17
Second set of data				
0	16.7	7.9	0.0	0.46
8.5	16.5	7.7	.0	.46
10.0	16.2	8.0	.0	.46
11.0	11.0	8.2	.0	.48
12.0	10.0	4.8	.1	.48
13.0	8.4	3.0	1.5	.35
14.0	8.0	1.5	5.7	.25

The oxidation of the ferrous ion can be catalyzed and affected by the presence of other ions. Data given by Lamb and Elder (1931), Weiss (1953), and Cher and Davidson (1955) show these effects. The positive catalytic effect of the cupric ion is especially interesting, pronounced effects being possible at quite low Cu^{++} concentrations.

Lamb and Elder (1931) reported that ferrous sulfate was oxidized more rapidly in a solution 0.023 molar in sodium pyrophosphate than in solutions containing sulfuric acid, but this effect may well be associated with the alkaline pH of phosphate solutions.

OCCURRENCE OF FERRIC IRON IN NATURAL WATERS

Theoretical and experimental data have been cited which indicate that many natural waters have pH and Eh values which preclude the presence of measurable amounts of ferrous iron. In many more natural waters, ferrous iron may be stable while the water remains in an environment out of contact with air but, on exposure to the air, the iron is wholly or partly oxidized to the ferric state.

In the pH range 5–8, the total amount of ferric iron that can remain in solution in the form of Fe^{+++}, $FeOH^{++}$, and $Fe\ (OH)^{+}_{2}$ ions is generally below 0.01 ppm. Therefore, measurable amounts of ferric iron in water in this range of pH must be either undissolved or combined in complex ions. In either case, the simplified theoretical approach is inapplicable.

SUSPENDED FERRIC IRON

A series of experiments demonstrated that synthetic water samples containing iron and other dissolved materials and having pH values near 7.0, lost iron by precipitation of ferric hydroxide. On standing for 11 to 17 days, nearly all this precipitate settled out of the solution and iron could not be detected in the supernatant liquid in two of the samples. Filtration through millipore filters having pore openings 0.45 microns in diameter lowered the iron content of these solutions to a point below the detection limit. Results of the settling-rate experiments were as follows:

Solution A, 330 ppm HCO_3^-, 8.0 ppm Fe, pH 7.0, specific conductance 1440 micromhos.

Time (days)	Fe present as suspended $Fe(OH)_3$ (ppm)
0	8. 0
. 8	1. 4
1.8	. 46
3.8	. 08
6.0	. 07
7.0	. 08
17.0	. 00

Solution B, 18 ppm HCO_3^- 0.4 ppm Fe, pH 7.3, specific conductance 76 micromhos.

Time (days)	Fe present as suspended $Fe(OH)_3$ (ppm)
0	----
2.0	0.28
2.9	.27
4.2	.20
5.2	.15
15.2	.01

Solution C, 48 ppm HCO_3^-, 1.0 ppm Fe, pH 7.4.

Time (days)	Fe present as suspended $Fe(OH)_3$ (ppm)
0	----
.8	1.1
2.1	.46
3.0	.25
11.0	.00

The rate of settling can be speeded by centrifuging. The centrifugation procedure was as follows: Samples were removed from the solutions after various periods of settling and centrifuged at 1500 rpm for periods of 5 minutes to 1 hour. Often this was not sufficient to settle all suspended material, and a longer period of settling followed by more centrifuging was required. Several solutions were treated in this manner. Amounts of iron present as suspended $Fe(OH)_3$ in one of these solutions after various periods of centrifuging and settling were as follows:

0.36 ppm after 1-day settling; centrifuging 5 min.
.05 ppm after 1-day settling; centrifuging 30 min.
.04 ppm after 2-day settling; centrifuging 20 min.
.02 ppm after 3-day settling; centrifuging 40 min.
.00 ppm after 5-day settling; centrifuging 40 min.

Similar treatment of 9 other solutions showed that all the suspended iron could be removed by centrifuging, and 5 days or less of settling.

The rate of settling of ferric hydroxide from the solutions is rather fast, and suspensions formed in this manner cannot be used to explain the origin of suspensions in natural samples, where concentrations at least as high as 0.3 ppm (and probably higher) are stable for months. Apparently the particle size of ferric hydroxide is finer in natural water than in the prepared samples. More data on particle size and better methods for laboratory preparation of the suspensions would be necessary for simulating the conditions of suspensions of natural samples.

Because these suspensions are metastable, their behavior is not accurately predictable. Table 9 shows data for six solutions made up in three pairs having essentially identical composition. The solutions were subjected to identical periods of settling and centrifuging.

TABLE 9.—*The nonpredictable behavior of ferric hydroxide suspensions*

Solution	pH	HCO_3^- (ppm)	F^- (ppm)	Initial Fe (ppm)	Final Fe as suspended $Fe(OH)_3$ (ppm)
30	7.9	522	4.0	8.0	0.06
30D	8.0	531	4.0	8.0	.11
32	5.6	20	4.0	8.0	.15
32D	5.4	23	4.0	8.0	.06
38	7.0	322	0	8.0	.04
38D	7.0	320	0	8.0	.00

Another means of removing suspended ferric hydroxide is filtration through a molecular membrane filter, Millipore type HA. These filters, capable of retaining particles as small as 0.5 micron in diameter, removed suspended ferric hydroxide from all but one of the prepared and natural samples investigated. The single exception, sample 1279, table 10, had an especially low pH and may have had a considerable quantity of dissolved ferric iron. It is interesting to note that Whatman No. 54 filters, typical of good, low-retentivity paper filters, do not remove all this material. Data for this filter are also included in table 10. Since the latter filters pass particles smaller than ca. 4 microns, they indicate roughly the particle size in these suspensions (0.5–4 micron).

TABLE 10.—*The filtration of ferric hydroxide suspensions*

[All solutions are prepared samples except 1708, 1690, and 1279, which are field samples]

Solution	Before filtration (ppm)	Suspended ferric hydroxide, in ppm, after filtration with a Millipore HA filter
A	0.08	0.00
B	.28	.005
C [1]	.46	.00
30D	.11	.00
32	.06	.00
33D	.04	.00
42	.01	.00
44	.01	.00
1708	.27	.00
1690	.03	.00
1279	36.0	21.2

[1] Solution C was also filtered through a Whatman No. 54 paper filter with a result of 0.37 ppm of suspended ferric hydroxide after filtration.

A few experiments were made to check the possibility of determining the amount of dissolved ferric iron in the presence of suspended ferric iron. The technique followed consisted of adding buffer-reductant to the aliquot, adjusting the pH to 5.0, and immediately adding the bipyridine to determine the color. This technique gave 0.00 ppm of iron for several synthetic samples that gave 0.00 ppm iron after centrifuging and/or filtering. However, the technique may not be valid for samples containing iron in colloidal suspension (particles smaller than 0.5 micron). The presence of complexing agents may also interfere with this procedure.

FERRIC COMPLEX IONS

Ferric iron is a powerful former of complexes. The complexes of iron with several different inorganic anions are mentioned in published literature. The anions generally present in natural water that would be most likely to have important effects include fluoride and phosphate; other ions such as chloride, sulfate, bicarbonate, and carbonate probably have less important effects.

A few experimental solutions were made up to study the effects of fluoride and phosphate in concentrations from 1.0 to 4.0 ppm. These solutions were made up with ferric chloride; they contained bicarbonate and had pH values from 5.3 to 9.1. It was possible to remove all the iron from the solutions by centrifuging or filtration, as was done with the solutions that did not contain the potential complexing ions. Under the conditions existing in these experiments, the complexing effects of the fluoride and phosphate ion evidently do not prevent precipitation of ferric hydroxide. At a lower pH ($\sim$2 or 3), however, the fluoride complex, at least, does affect the behavior of iron. At these lower pH levels, ferric ions would be available in the solution to be formed into complexes. At higher pH, the $Fe(OH)_3$ form is the stable one, and ferric ions are present in amounts well below the detection limit.

Babko and Kleiner (1947) report dissociation constants for ferric fluoride complexes FeF^{++}, and FeF_2^+ as 5×10^{-6} and 0.4×10^{-4}, respectively. Their experiments were made in a strongly acid solution ($pH \sim 1$) and imply essentially complete complexing, even when F^- concentration is in the low range common in natural water.

Equilibrium constants for the chloride complexes (table 1) indicate that about half the ferric ions would be converted to $FeCl^{++}$ at a concentration in the vicinity of 1,000 ppm of Cl. Again, for either Fe^{+++} or $FeCl^{++}$ to be present in amounts over 0.01 ppm, the pH would have to be low.

Table 11 contains some data on the behavior of iron and changes in Eh observed in solutions containing various amounts of chloride. Carbon dioxide was bubbled in the distilled water while the solutions were being prepared. After the addition of HCO_3^- and Cl^-, the pH was brought up to 6.0 with 1 normal Na_2CO_3. The iron was added after the above pH was obtained. Solutions *A*, *B*, *C* started to be-come cloudy after 15 minutes of standing. Solutions *D* and *E* remained clear until the next day when they became cloudy. The presence of chloride in the higher concentration in these studies seems to retard the oxidation rate of ferrous iron, but the Fe^{++} was no longer detectable after about 6 days. The Eh of these solutions after the oxidation of ferrous iron, however, seemingly was related to the amount of chloride present. Solutions containing the most chloride had the highest final Eh. The latter effect may be the result of decreasing activity coefficients in the more concentrated solutions, or may stem from anomalous other effects of the presence of much dissolved material. More work would be needed to explain this effect completely. A series of solutions similar to those in table 11

TABLE 11.—*The stability of ferrous iron in the presence of chloride*

[All solutions have an initial pH of 6.0 and contain 15 ppm of Fe^{++} and 100 ppm of HCO_3. Parts per million of Cl^- contained in solutions as follows: A, 0.00; B, 10; C, 1,000; D, 10,000; E, 50,000]

Time (days)	pH	Fe^{++} (ppm)	Eh (volts)
Solution A			
0	6.0	15	----------
.1	6.5	8.2	0.278
1.0	6.3	.30	.417
3.0	6.5	.02	.431
5.9	6.4	.00	.431
Solution B			
0	6.0	15	----------
.1	6.4	8.5	0.295
1.0	6.2	.43	.438
3.0	6.4	.04	.441
5.9	6.3	.00	.444
Solution C			
0	6.0	15	----------
.1	6.5	8.5	0.295
1.0	6.2	.17	.455
3.0	6.5	.02	.455
5.9	6.5	.00	.467
Solution D			
0	6.0	15	----------
.1	6.5	13.5	0.295
1.0	6.3	6.5	.402
3.0	6.4	.08	.485
5.9	6.3	.00	.527
Solution E			
0	6.0	15	----------
.1	6.2	14	0.301
1.0	6.2	7.0	.402
3.0	6.4	.54	.485
5.9	6.4	.00	.527

but containing no iron did not exhibit an increased Eh at high chloride concentrations.

No work was done on ferrous complexes, another aspect of complexing that probably is important in natural-water chemistry. Certain organic molecules may form complexes with ferric iron or ferrous iron. Probably some of these complexes are chelates, and their behavior is controlled by the organic part of the complex. No work has been done with these materials.

LABORATORY PROCEDURES

The iron determinations were made by the bipyridine method described by Moss and Mellon (1942) and a Beckman Model B spectrophotometer. In general, the methods were similar to or the same as those commonly used with water by the Geological Survey. For determining ferrous iron in the presence of suspended ferric iron, the aliquot was kept at a pH of 5.0 to avoid any possibility of solution of ferric iron, and the color was read immediately after addition of bipyridine. The procedure has not been studied sufficiently to be certain it is un-affected by suspended ferric iron under all conditions.

The optical density-iron concentration curve was checked while the experiments were in progress with a series of $FeCl_3$ standards. The latter were prepared by dissolving clean, dried iron wire in HCl.

Eh and pH measurements were made on Beckman Model H2 and N pH meters, using a calomel reference electrode and a platinum electrode for the Eh measurements. The value Eh=0.246 volts was used for the calomel electrode (ZoBell, 1946).

The pH meter was calibrated for Eh measurements with a solution M/300 in $K_3Fe(CN)_6$, M/300 in $K_4Fe(CN)_6$, and M/10 in KCl. This solution has an Eh of 0.430 volts at 25° C (ZoBell, 1946).

CONCLUSIONS

The theoretical considerations and the experiments here described lead to the following generalizations:

1. The amounts and kinds of dissolved ions or molecules containing iron in the ferrous and ferric states are related to the pH and Eh of the water in which they occur. Quantitative expressions of these relationships can be made using the Nernst equation and appropriate equilibrium constants.
2. Ferric iron can be present in true solution in amounts greater than 0.01 ppm only at pH levels below about 5.0. Hence, in most natural waters, iron in true solution must be mostly in the ferrous state. The ferrous iron is oxidized to ferric when the waters are exposed to air. This reaction is slow in strong acid, but can be rapid in the normal range of pH for natural water.

3. The Nernst equation, field pH, and iron content of waters provide a basis for estimating Eh of ground waters in their natural environment, a property that cannot be measured with present equipment.
4. Waters that are in contact with air, such as surface waters and stored samples of ground waters, may contain ferric iron in a metastable suspension. Particle size is often greater than the upper limit for the colloidal state, and iron in such waters can be removed by centrifuging or filtration to a point where the remainder is below detection.
5. Inorganic complex ions with ferric iron affect the behavior of iron at low pH. The pH values involved for fluoride and chloride complexes are considerably below the range of bicarbonate-carbon dioxide buffering and are not generally attained in natural water.
6. The effect of organic complexing or chelating agents is probably important but has not yet been studied in this investigation.

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