Some Chemical Relationships Among Sulfur Species and Dissolved Ferrous Iron

JOHN D. HEM

CHEMISTRY OF IRON IN NATURAL WATER

A discussion of ferrous iron activity in the presence of several species of sulfur, under a variety of Eh-pH conditions

UNITED STATES DEPARTMENT OF THE INTERIOR

FRED A. SEATON, *Secretary*

GEOLOGICAL SURVEY

Thomas B. Nolan, *Director*

CONTENTS

ILLUSTRATIONS

III

CHEMISTRY OF IRON IN NATURAL WATER

SOME CHEMICAL RELATIONSHIPS AMONG SULFUR SPECIES AND DISSOLVED FERROUS IRON

By John D. Hem

ABSTRACT

Sulfur species most likely to occur in natural water are HS^{-1}, H_2S, HSO_4^{-1}, and SO_4^{-2}; and free sulfur (S^0) may be a stable form. The stability fields for these five species are shown on an Eh-pH diagram. A second Eh-pH diagram shows the range of conditions under which iron activity could amount to 10^{-7} molal or more in the presence of solid-phase ferrous sulfide and a total dissolved sulfur content 10^{-5} molal, in the absence of bicarbonate. Reactions involving oxidation or reduction of sulfur are slow but may be speeded by biochemical influences.

If equilibrium is established, natural water containing a few hundred ppm (parts per million) of SO_4^{-2} and HCO_3^{-1} could contain over 10 ppm of iron only if pH is less than about 6.1 over a rather wide Eh range. Some ground-water samples are not at equilibrium, however. Wells may obtain water from several poorly interconnected zones in which Eh, iron, and sulfur content differ.

Oxidation of pyrite evidently can be an important source of iron in ground water. The changes in Eh with depth below the water table and the fluctuation of the water table may result in stratification of iron content in ground water and in erratic changes in iron content of water from wells; they may cause iron deposits to form in aquifers and wells. Such deposits could reduce the capacity of wells to yield water and might interfere with ground-water movement.

INTRODUCTION

This discussion is one of a series of research studies in the chemistry of iron in natural water conducted by the U.S. Geological Survey. The purpose of the studies is to determine the chemical and biochemical principles and processes that control the forms and amounts of iron that occur in natural surface and underground water, and to relate these chemical processes to hydrology. Understanding the relation of water to its environment in the hydrologic cycle is imperative to effective development of water resources and waste disposal.

Natural water contains certain ions which affect the behavior of iron directly or indirectly. For example, the erratic changes in iron content of ground water from adjacent wells are common. Also, the iron content may vary with time as the well is pumped, with pumping rate, and other factors. Some of these changes can be better understood with knowledge of the chemical behavior of iron in the presence of sulfur or carbon dioxide. The relation between various forms of iron and sulfur are examined and evaluated in this report.

The manuscript has been examined and reviewed by colleagues of the author and by Dr. H. S. Puleston and Dr. G. H. Splittgerber of

the Department of Chemistry, Colorado State University, Fort Collins, Colo.

CHEMICAL EQUILIBRIA INVOLVING SULFUR AND IRON IN GROUND WATER

The chemical relations among ferrous and ferric iron, pH, Eh, and anions derived from carbon dioxide in solution have been examined and evaluated by application of chemical thermodynamics (Hem and Cropper, 1959; Hem, 1960). Certain forms of sulfur affect the behavior of iron in natural water; therefore, the relation between sulfur and iron should also be examined and evaluated.

Sulfur is present in natural water as an anion. The oxidation state, however, may range from S^{-2} in sulfide to S^{+6} in sulfate. The form in which anions containing sulfur occur in solution is pH dependent. For example, at low pH, reduced sulfur may be present as undissociated H_2S; at high pH, as HS^{-1}; and at very high pH, as S^{-2}. Oxidized sulfur may be present as HSO_4^{-1} in strong acid, but the SO_4^{-2} form prevails in the usual pH ranges of natural water. These five are the common dissolved sulfur species. Many less-common species exist, in which sulfur has intermediate oxidation states; for example, thionate, thiosulfate, and sulfite. Some of these less-common species have been reported in analyses of water from thermal springs. However, thermodynamic calculations indicate that in potable water at 25° C at 1 atmosphere of pressure and in the pH range from 4 to 9, the less-common sulfur species would not be stable and, therefore, are not likely to occur.

Sulfides of ferrous iron are common minerals and may be sources of iron as well as of various anionic forms of sulfur in ground-water systems. The common sulfide minerals pyrrhotite (FeS) and pyrite (FeS_2), when not subject to oxidation or reduction, are commonly less soluble than siderite ($FeCO_3$). Thermodynamic data given by Latimer (1952, p. 222) indicate that the solubility product for ferrous sulfide is 4×10^{-19}; for pyrite, about 10^{-30}; and for siderite, 2.11×10^{-11}. The behavior of the sulfides is affected by pH and by oxidation and reduction. Both the cationic and anionic parts of these sulfide minerals are subject to oxidation; thus the behavior of these sulfides is different from that of siderite in oxidizing systems involving water.

Sulfur-ferrous iron equilibria in solution can be simply described by the Eh-pH or stability-field diagram. The general techniques for preparing such a diagram were developed by Pourbaix (1949) and have been extended to systems very similar to the ones of interest here by several investigators. Discussions by Krumbein and Garrels (1952) and by Huber and Garrels (1953) are particularly pertinent. The relations among the ferrous and ferric ions and hydroxides were

presented in a stability-field diagram by Hem and Cropper (1959) in a report on the chemistry of iron in natural water. Garrels and Naeser (1958) have discussed dissolved sulfur species in detail. The application of redox potentials to evaluation of reactions involving sulfur is complicated because oxidation or reduction of sulfur through chemical agencies alone is commonly very slow. In ground-water environments, the reaction may be rapid if the right kinds of bacteria are present, but sulfate or sulfide commonly exists for a long time at Eh levels where they are not expected to be stable. Although in most ground-water systems a prolonged contact between water and solid-phase minerals can be assumed, a chemical equilibrium cannot be assumed. Therefore, in the application of chemical thermodynamics, the sulfate-sulfide ratios in a water cannot be used to compute the Eh. Some useful generalizations can be made, however, from studies of sulfur potentials if the limitations are kept in mind.

The sulfur in pyrrhotite is in the S^{-2} form, which is a more reduced form than the S_2^{-2} in polysulfide. The assignment of an oxidation state to S_2^{-2} is arbitrary because the difference between between S_2^{-2} and S^{-2} is a result of change from polar to covalent bonding. Thermodynamic data are available, however, to evaluate this change; thus the Eh-pH conditions in which each of the two sulfide minerals will predominate can be predicted.

Equilibrium constants (Latimer, 1952, p. 71, 74) needed to evaluate the systems and free-energy data (Latimer, 1952, p. 72, 221) are given in the following table: .

Equilibrium constants

Chemical equilibrium		K
H_2S aq$\rightleftharpoons HS^{-1} + H^{+1}$	-	1.1×10^{-7}
$HS^{-1} \rightleftharpoons S^{-2} + H^{+1}$		1×10^{-14}
$HSO_4^{-1} \rightleftharpoons SO_4^{-2} + H^{+1}$		1.26×10^{-2}

Free-energy data

[State: aq, aqueous; c, crystal; 1, liquid]

Ionic species	State	ΔF° (kcal)
Fe^{+2}	aq	-20.30
FeS	c	-23.32
FeS_2	c	-39.84
S^{-2}	aq	22.1
S_2^{-2}	aq	21.8
H_2S	aq	-6.54
HS^{-1}	aq	3.01
HSO_4^{-1}	aq	-179.94
SO_4^{-2}	aq	-177.34
H_2O	1	-56.69
S^0	c	0
SO_3^{-2}	aq	-116.1
$S_2O_3^{-2}$	aq	-124.0
HSO_3^{-1}	aq	-126.0

STABILITY FIELDS FOR DISSOLVED SULFUR SPECIES

The dissociation constants for hydrosulfuric acid permit the computation of fields of stability for H_2S, HS^{-1}, and S^{-2}:
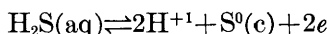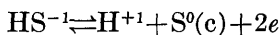
$$H_2S \rightleftharpoons HS^{-1} + H^{+1}, K_1 = 1.1 \times 10^{-7}$$
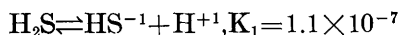
$$\frac{[HS^{-1}]}{[H_2S]} = \frac{1.1 \times 10^{-7}}{[H^{+1}]}$$

Where the ratio on the left has a value of 1 ($[HS^{-1}] = [H_2S]$), $[H^{+1}]$ will be 1.1×10^{-7}, and $pH \approx 7.0$. A line at this pH separates the fields of dominance of HS^{-1} and H_2S in figure 6. A similar computation for the second dissociation shows that S^{-2} cannot predominate at any pH below 14; hence, no S^{-2} field appears in figure 6.

Dissociation constants indicate that sulfuric acid is much stronger than hydrosulfuric acid. For sulfuric acid, the second dissociation constant is 1.26×10^{-2}, which gives a pH of 1.9 as the boundary between HSO_4^{-1} and SO_4^{-2} fields. Undissociated sulfuric acid would not predominate at any pH greater than 0.

The positions of other boundaries in figure 6 were computed from the following oxidation couples:

$$HS^{-1} \rightleftharpoons H^{+1} + S^0(c) + 2e$$

$$H_2S(aq) \rightleftharpoons 2H^{+1} + S^0(c) + 2e$$

$$HS^{-1} + 4H_2O \rightleftharpoons SO_4^{-2} + 9H^{+1} + 8e$$

$$S^0(c) + 4H_2O \rightleftharpoons SO_4^{-2} + 8H^{+1} + 6e$$

$$S^0(c) + 4H_2O \rightleftharpoons HSO_4^{-1} + 7H^{+1} + 6e$$

Boundaries separating the stability fields for sulfur species that may be expected in natural water are shown as solid lines in figures 6. The ferrous-ferric boundary is shown as a dotted line and is from a diagram given by Hem and Cropper (1959).

Other forms of sulfur for which free-energy data are available were also examined. Besides the species previously indicated as common, free sulfur seems to be a stable intermediate product. Other species of sulfur do not have fields of stability. The existence of solid-phase free sulfur is hypothetical (see p. 62). The computation process of the HS^{-1} to SO_4^{-2} boundary, which is based on the third couple given above, is as follows:

Free-energy values given on page 59 are used to compute the net change in standard free energy in the oxidation of 1 mole of HS^{-1}.
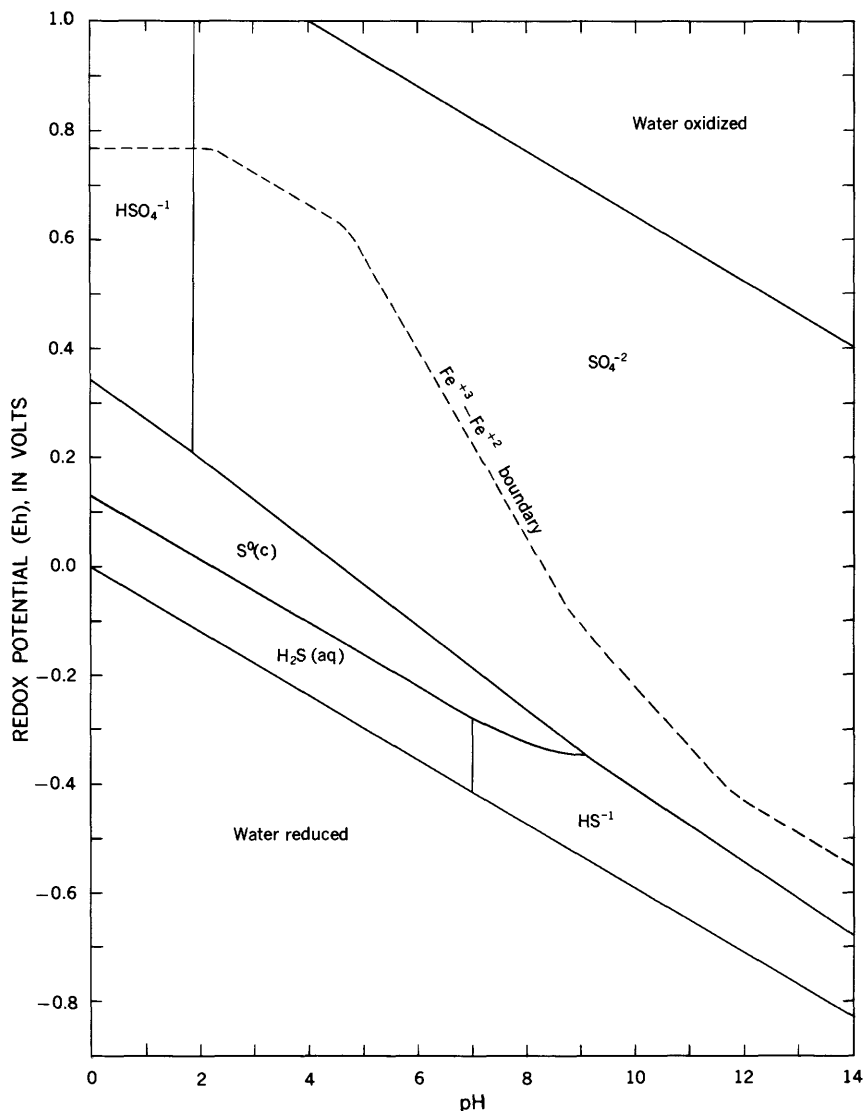
FIGURE 6.—Fields of stability of sulfur species likely to occur in natural water.

Thus, $\Delta F° = -177.34 - 4(-56.69) - 3.01 = 46.41$ kcal (kilocalorie).
The result is used to compute the standard potential $E°$:

$$E° = \frac{\Delta F°}{8(23.06)} = 0.25v$$

The Nernst equation for the system is:

$$Eh = E° + \frac{0.0592}{8} \log \frac{[SO_4^{-2}][H^{+1}]^9}{[HS^{-1}][H_2O]^4}$$

539368 O–60—2

The activities of SO_4^{-2} and HS^{-1} must be equal along the boundary sought, and water is assumed to be present at unit activity. The terms then cancel out, and the equation becomes

$$Eh = 0.25 - 0.0666 \ pH$$

which fixes the boundary between HS^{-1} and SO_4^{-2} in the pH range where HS^{-1} is dominant. This range is shown on figure 6 to be between pH 7.0 and pH 14; hence, this equation is useful only between pH values of about 7.0 and 14. Similar computations with the other couples show that for a pH of less than 9.0, free sulfur appears as an intermediate stage in the oxidation. Thus, the area of the Eh-pH diagram is occupied by five different sulfur species.

Thermodynamic computations for other stages of sulfur oxidation show that the oxidation of HS^{-1} or H_2S to such forms as polysulfide (S_2^{-2}), thiosulfate ($S_2O_3^{-2}$), or sulfite (SO_3^{-2}) occurs at a higher oxidation potential than the oxidations of HS^{-1} or H_2S to free sulfur and to sulfate. Hence, these other ions do not have stability fields in figure 6. The other sulfur species may be metastable, but sulfide probably would be partly oxidized to free sulfur or completely oxidized to sulfate if oxidation is speeded by bacterial action. Although the sulfur species may not reach chemical equilibrium because of slowness and incomplete reversibility of some of the systems being considered, figure 6 is useful in at least an approximate sense, and helps explain why the intermediate oxidation states do not commonly occur.

Figure 6 demonstrates that sulfate is the only stable form of sulfur in the ferric stability region. Ferric sulfides, therefore, do not have stability fields.

Although free sulfur is shown as a stable phase in figure 6, its stability is partly a result of assumptions used in the computations, and its significance in a ground-water system is questionable. The boundaries of the sulfur field were drawn at points where S^0 and the other sulfur species were at equal activity. Because the free sulfur is a solid phase, it would be represented nominally at unit activity in thermodynamic computations. Where all sulfur species are present at unit activity, no difficulties arise. However, if the diagram is applied to a natural water in the potable concentration range, the total amount of dissolved sulfur species will be much less than unit activity. If an equilibrium between S^0 and the other sulfur species is ultimately reached, the activity of S^0 would then be unity. Whether or not such an equilibrium could be attained in the presence of very small amounts of dissolved sulfur species is questionable. Using unit activity for S^0 causes the S^0 (crystal) field to decrease in size as the dissolved sulfur content of the system is decreased. When the total

activity of dissolved sulfur species is 10^{-5} molal as in figure 7, the S^0 field would be very small. Possibly, the solid-phase sulfur area on figure 6 should be considered as an "instability" region for the other four sulfur species. Also, sulfur is soluble in solutions containing sulfide (forming polysulfides) and this was not considered in making the diagram.
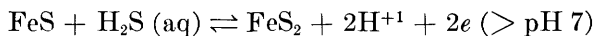
The reduction of sulfate in ground water probably is complete from S^{+6} to S^{-2}. However, free sulfur is not uncommon as a product of the oxidation of H_2S in the air, and colloidal sulfur may occur in water as the result of a partial oxidation of sulfides.

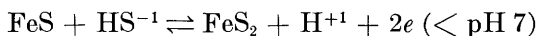### SOLUBILITY DIAGRAM FOR FERROUS SULFIDES

The relations at equilibrium among some of the dissolved sulfur species, the iron in solution, and the solid-phase ferrous sulfides present can also be expressed in an Eh-pH diagram. For this diagram, a system similar to that in a ground water can be assumed as the limiting condition. Most of the reactions among iron and sulfur species are rapid enough for equilibrium conditions to be reached. For the diagram (fig. 7), the activity of dissolved iron was assigned as 0.01 ppm (the lower limit of detection in routine analyses) or about 10^{-7} molal.   The assignment of a molal value for total activity of sulfur was also necessary. Information on amounts of reduced sulfur species is missing from most chemical analyses of water. If reduced sulfur is present, the odor of H_2S is noticeable, however, and usually is reported in qualitative terms. A few tenths parts per million of H_2S in water gives a noticeable odor. For this analysis, the activity of sulfide in solution was assigned as 0.3 ppm, which is equivalent to 10^{-5} molal and is near the limit of detection of H_2S by odor. The presence of an excess of solid-phase ferrous sulfides, either pyrite or pyrrhotite, was assumed.

The pyrite stability field in figure 7 does not coincide with the stability fields for HS^{-1}, H_2S, and S^0 in figure 6. Otherwise, the two illustrations are closely related.

In preparing the diagram, the first step is to establish the fields of stability of the two sulfide minerals. In the presence of $\Sigma H_2S + HS^{-1} + S^{-2}$ activity $= 10^{-5}$, the following equilibria will govern the system:

$$FeS + H_2S \text{ (aq)} \rightleftharpoons FeS_2 + 2H^{+1} + 2e \;(> pH\ 7)$$

and

$$FeS + HS^{-1} \rightleftharpoons FeS_2 + H^{+1} + 2e \;(< pH\ 7)$$

Values of $\Delta F°$ for these reactions are -9.98 and -19.53 kcal, respectively. Substituting in the equation
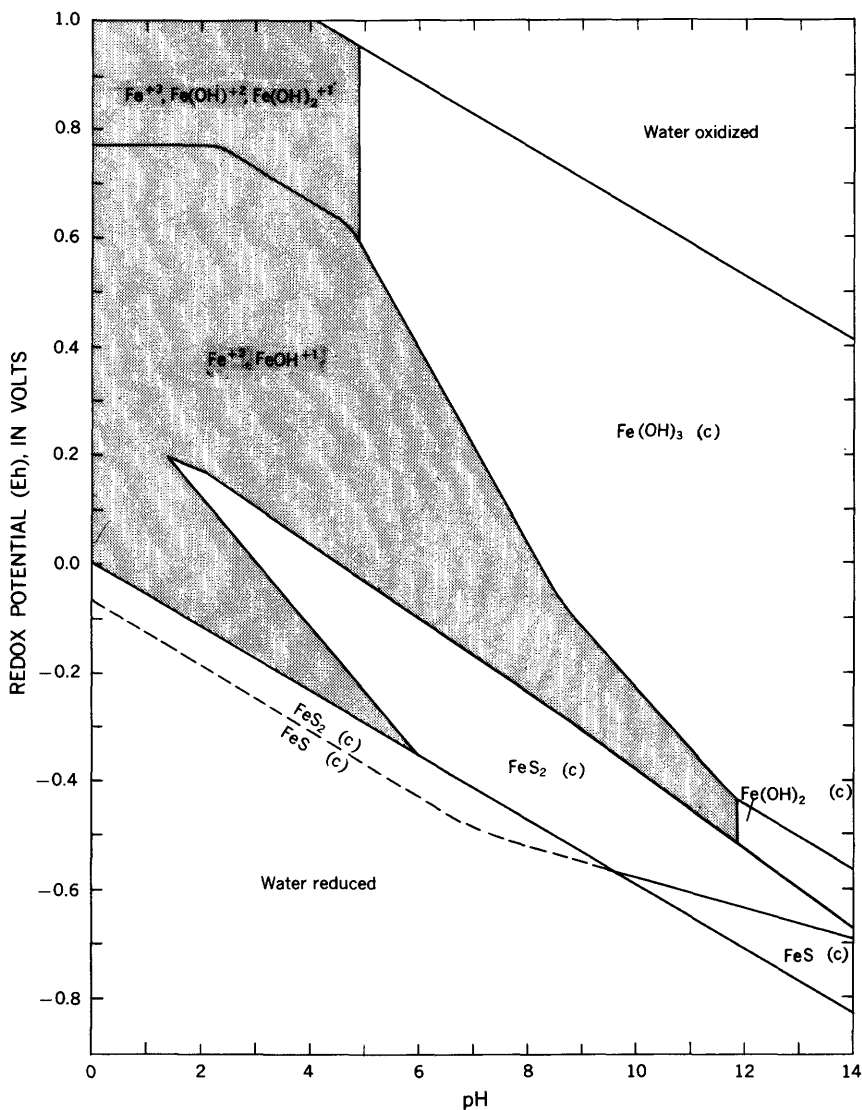
$$E° = \frac{\Delta F°}{2(23.06)}$$

FIGURE 7.—Eh–pH region in which dissolved iron activity can exceed 0.01 ppm. Total sulfur activity, 10^{-5} molal; carbon dioxide, bicarbonate, and carbonate absent.

we obtain for $E°$, -0.22 v and -0.42 v, respectively. For the position of the FeS–FeS_2 boundary between pH 0 and 6, the Eh can be obtained from the Nernst equation for the first reaction:

$$\text{Eh} = -0.22 + \frac{0.0592}{2} \log \frac{[FeS_2]\,[H^{+1}]^2}{[FeS]\,[H_2S]}$$

Substituting the assigned value of 10^{-5} for $[H_2S]$ and assuming the two solid-phase minerals to be present in equal and unit activity at the boundary, the equation is simplified to:

$$Eh = -0.22 - 0.0592 \; pH + 0.15$$

This equation defines the boundary between pyrite and pyrrhotite fields in figure 7 from pH 0 to 6. A similar computation for the pH range between 8 and 14 gives the equation

$$Eh = -0.42 - 0.0296 \; pH + 0.15$$

which defines the boundary between the pyrite and pyrrhotite fields. In the region of pH 7, the two boundary lines are joined in a smooth curve because the transition from H_2S to HS^{-1} is gradual rather than abrupt.

The FeS–FeS_2 boundary can also be computed from either of the two equations alone by substituting values for $[HS^{-1}]$ or $[H_2S]$ computed from the dissociation constant and the pH and the total sulfide. This technique gives more exact values near points where the boundary changes in slope.

For pH of less than 10, the position of the boundary between the two ferrous sulfides on figure 7 is actually outside the region of stability for water. Therefore, pyrrhotite is not a stable form in contact with water under 1 atmosphere pressure at 25° C unless the pH is very high (more than 10) and Eh very low. These conditions are very rare in natural solutions.

Establishing the position of the upper (oxidizing) limit for pyrite in contact with natural water is the next step. Oxidation of pyrite can progress in several different ways. However, trial calculations demonstrate that complete oxidation without intermediate species is most probable. The direct oxidation of pyrite to give Fe^{+2} and SO_4^{-2} in solution can be written:
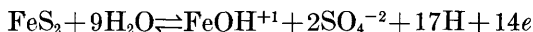
$$FeS_2 + 8H_2O \rightleftharpoons Fe^{+2} + 2SO_4^{-2} + 16H^{+1} + 14e$$
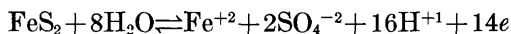
The standard free-energy change $\Delta F°$ for this reaction is 118.38 kcal, and the standard potential $E°$ is 0.37 v. Applying the Nernst equation gives the relation:

$$Eh = 0.37 - 0.030 - 0.042 - 0.0676 \; pH$$

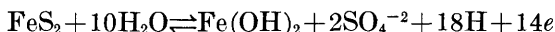Where $[Fe^{+2}] = 10^{-7}$ and $[SO_4^{-2}] = 10^{-5}$.

This equation represents the boundary at which pyrite is oxidized to an extent sufficient to give at equilibrium an iron activity of 10^{-7} molal in solutions in contact with the pyrite.

From pH 8.7 to 11.6, the dissolved iron is mostly in the form $FeOH^{+1}$; and above pH 11.6, solid $Fe(OH)_2$ is the stable form (Hem and Cropper, 1959). The equations for the oxidation of pyrite to give these forms of iron are:

$$FeS_2 + 9H_2O \rightleftharpoons FeOH^{+1} + 2SO_4^{-2} + 17H + 14e$$

and

$$FeS_2 + 10H_2O \rightleftharpoons Fe(OH)_2 + 2SO_4^{-2} + 18H + 14e$$

The Eh–pH relations, derived as before, give a slight steepening of the slope of the boundary along which oxidation of pyrite takes place to form the hydroxide complex and solid $Fe(OH)_2$.

The sulfur of pyrite is in the S_2^{-2} form, which represents a greater degree of oxidation than that of the S^{-2} form. Figure 6 indicates that S^{-2} is the stable form for sulfur species in the greater part of the pyrite field of figure 7; therefore, pyrite would be reduced in the presence of H^{+1}. Writing this reaction as an oxidation to conform with couples previously shown:
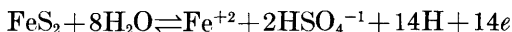
$$Fe^{+2} + 2H_2S(aq) \rightleftharpoons FeS_2 + 4H^{+1} + 2e$$
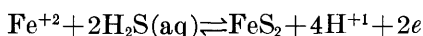
$$\Delta F^\circ = -6.46 \text{ kcal}$$

$$E^\circ = -0.14v$$

$$Eh = -0.14 + 0.21 + 0.30 + 0.119 \text{ pH}$$

This equation gives the most steeply sloping boundary of the FeS_2 field shown on figure 7, along which pyrite would be in equilibrium with a solution 10^{-5} molal in H_2S and 10^{-7} molal in ferrous iron.

Below pH 1.9, the equation for pyrite oxidation is:

$$FeS_2 + 8H_2O \rightleftharpoons Fe^{+2} + 2HSO_4^{-1} + 14H + 14e$$

Only a small part of the pyrite stability field extends below pH 1.9.

In a part of the stability field of FeS_2 (crystal), figure 6 indicates that free sulfur could be a stable phase. Here oxidation of pyrite would yield ferrous ions and sulfur. This reaction would be:

$$FeS_2 \rightleftharpoons Fe^{+2} + 2S^0 + 2e$$
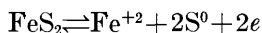
$$\Delta F^0 = 19.54 \text{ kcal}$$

$$E^0 = 0.42 \text{ v}$$

$$Eh = 0.42 + \frac{0.0592}{2}\log[Fe^{+2}] = 0.21$$

(The value for activity of sulfur is taken as unity.)   This line has zero slope because the reaction does not involve hydrogen ions.   It falls outside the pyrite stability field and, hence, does not appear in figure 7.

In figure 7, the Eh-pH regions where iron activity would be 0.01 ppm or more are shaded.   The assumed total activity of all forms of dissolved sulfur is 10^{-5} molal, equivalent to about 0.3 ppm H_2S or about 1 ppm sulfate.   Carbon dioxide, bicarbonate, or carbonate are absent from this system.   Because of the possible existence of forms of sulfur not in equilibrium, the diagram should be interpreted with some caution; but the following facts may be pointed out:

Pyrite has a very low solubility; therefore, if equilibrium has been reached, a measurable amount of iron is not likely to be in a solution containing sulfide.   Although equilibrium may often be attained in aquifers, some wells do yield water containing both iron and sulfide. Such wells may obtain water from imperfectly communicating layers; water in one layer may contain dissolved iron and water in the other may contain reduced sulfur.   These waters are mixed in or near the well bore and may be pumped out before chemical equilibrium can be reached.   The only set of Eh-pH conditions for which reduced sulfur and ferrous iron both could be stable in solution in detectable amounts is in the part of the H_2S field in figure 6 that coincides with the ferrous field in figure 7.   This part, which lies to the left of pH 6, probably is rarely attained in natural water.   However, some acid spring water contains both Fe^{+2} and H_2S and therefore, may have the Eh and pH required to lend stability to this combination.

The ferrous hydroxide stability field is small in figure 7 and would become smaller in the presence of more sulfur.   The ferric hydroxide field occupies most of the region where ferric iron is the stable form. The low solubility of ferric hydroxide prevents iron in solution from reaching a concentration of 0.01 ppm in a large part of figure 7.

Most natural waters contain more than 1.0 ppm of sulfate and practically all of them contain dissolved carbon dioxide, and bicarbonate and carbonate ions.   Figure 8 shows the Eh and pH at which a solution containing moderate amounts of dissolved sulfur and carbonate species would be in equilibrium with dissolved iron activities ranging from 0.01 to 100 ppm.   The total sulfur activity chosen for plotting figure 3 is 10^{-3} molal, equivalent to 96 ppm as SO_4^{-2}, and the total carbonate species activity is 5×10^{-3} molal, equivalent to 305 ppm as HCO_3^{-1}.   The positions of the lines representing total iron activity were determined from the equations used for figure 7, the relation:

$$\frac{[Fe^{+2}] \ [HCO_3^{-1}]}{[H^{+1}]} = 4.7 \times 10^{-1}$$
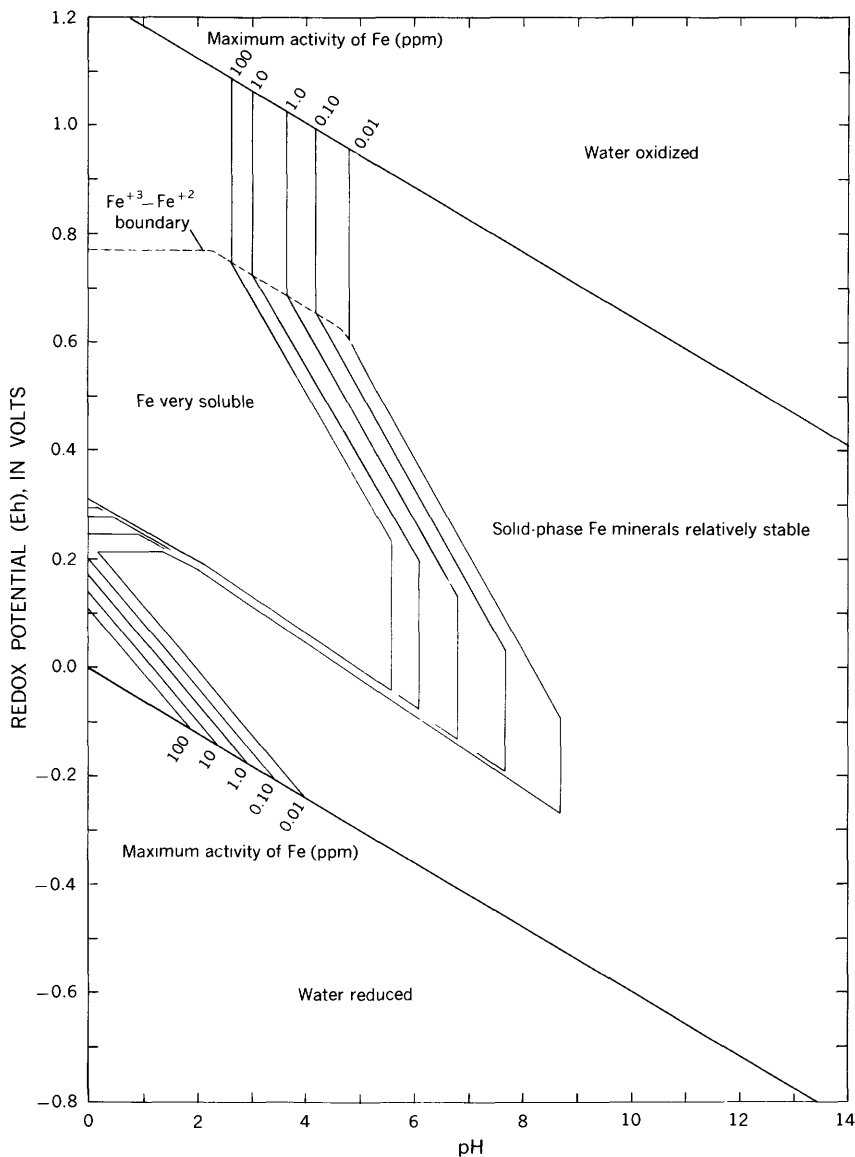
FIGURE 8.—Activity of dissolved iron related to Eh and pH in the presence of dissolved sulfur and dissolved carbonate.

and solubility calculations for ferric species below pH 5.0 (Hem, 1960).

The stability fields of specific solid-phase iron minerals are not given in figure 8, but the calculations assume the presence of ferric hydroxide, siderite, and pyrite.

Comparison of figure 8 with figure 7 demonstrates the effect of bicarbonate on the behavior of dissolved iron.   The deep penetration of the iron-solubility region into the alkaline reducing area in figure 7 is cut off near pH 9 in figure 8 by the low solubility of ferrous carbonate. The solubility of ferrous carbonate, however, increases with decreasing pH.   The effects of pH and Eh on the solubility of ferric hydroxide have already been described (Hem and Cropper, 1959).

The effect of increasing total sulfur activity from 10^{-5} molal in figure 7 to 10^{-3} molal in figure 8 is most marked where pyrite is reduced at low pH to give Fe^{+2} and H_2S.   Increasing the total dissolved sulfur activity to 10^{-3} molal eliminates much of the region where more than 0.01 ppm of iron could be present when all the sulfur is in the form of H_2S.   The effect of increased sulfate on the position of the upper boundary of the FeS_2 field along which oxidation to Fe^{+2} and SO_4^{-2} occurs is relatively minor, except at a pH of less than 1.   At this very low pH, the oxidation goes through an intermediate stage to produce solid-phase sulfur and Fe^{+2}.

The close spacing of the 0.01 ppm and 100 ppm iron-activity lines along the FeS_2 oxidation boundary suggests that pyrite would be readily oxidized if acted upon by water with a high enough Eh. Pyrite oxidation is a source of ferrous iron in many natural groundwater environments.

Although figure 8 is useful as a guide to the chemical factors that affect the iron content of natural water, the usefulness of this diagram is limited because selection of single sulfur and bicarbonate values is necessary and because assumption of equilibrium and absence of complexing is required.   Nonequilibrium conditions in natural water will result in deviations from the predicted condition.   An infinite number of such diagrams would be required to represent all possible conditions in natural water.   The diagram is not a good representation of such systems in a few respects; for example, a change in pH is often accompanied by changes in total carbonate activity.   In spite of its limitations, however, figure 8 does show that the presence of a few hundred ppm each of bicarbonate and sulfate in solution considerably restricts the Eh-pH region where high iron concentration (more than 10 ppm) can be expected at equilibrium.   Such iron content would be likely only for a pH of less than 6.1, although a rather wide range of Eh is possible.   The data available on pH and Eh of iron-bearing ground waters substantiate this general conclusion.   Analyses of several hundred iron-bearing ground waters from all parts of the United States have been examined.   In some of these waters, supersaturation seemed to be attained, usually with respect to $FeCO_3$ but sometimes with respect to FeS_2.

EFFECT ON IRON CONTENT OF CHANGES IN OXIDATION STATE OF SULFUR

Figures 6 and 7 help explain other features of the observed be-havior of both sulfur and iron in natural water. In the pH range from 4 to 9, any system in contact with air will have a redox potential well within the sulfate, or oxidized, region. Sulfate is therefore the stable form of sulfur in surface water and, because ground-water replenishment consists largely of water having had previous contact with air, sulfate is to be expected also in ground water. Redox potentials required to convert sulfur to sulfate are less than those required to oxidize iron to the ferric state. Both ferrous and ferric sulfates are highly soluble. Hence, no particular effect on iron content is to be expected in water containing only sulfate.

Reduction of sulfate to sulfide may remove iron from solution by precipitation of ferrous sulfide, and subsequent oxidation of such sulfides may return iron to solution.

SULFATE REDUCTION

In environments where oxygen is severely depleted, as in some water-logged soils and especially in muds deep below ocean or lake surfaces, sulfate reduction commonly occurs. Figure 6 indicates that the max-imum Eh at which this reduction will be sustained at pH 4 and 9 would be 0.04 and −0.34 v, respectively. Chemical reduction of sulfate, however, is a very slow process. In the laboratory, Huber and Garrels (1953) produced systems in which the Eh was low enough for sulfate reduction to occur, but they could not observe the reaction taking place.

The effect of bacteria on the rate of the reduction of sulfate is discussed in many places in the literature. The action of the bacteria, however, is not clearly understood. The weight of opinion suggests that the reduction requires bacterial action to proceed at a fast rate.

Sulfate reduction is endothermic; that is, a supply of energy is required to sustain the reaction. One mechanism that has often been postulated as a source of this energy is the simultaneous oxidation of a hydrocarbon such as methane. Thermodynamic calculations in-dicate that the Eh and pH conditions at which methane is oxidized to carbon dioxide, bicarbonate, or carbonate, are in the region of figure 6 where reduced sulfur species are stable; evidently sulfate reduction accompanied by hydrocarbon oxidation is a possible re-action that is speeded by certain anaerobic species of bacteria.

The available Eh measurements for ground-water systems indicate that values low enough for sulfate reduction to occur are not frequently observed. Such values would be expected only for ground-water

systems in which the sediments contain organic matter, bacterial colonies of the right kind exist, and oxygen is nearly excluded.   Nevertheless, ground waters that apparently have undergone sulfate reduction are common in some places.   These waters are commonly identifiable by their very low sulfate content.   Rarely, however, do they have a sulfide content that approaches equivalence with the sulfate content that was lost.

When sulfides have once been produced, they are metastable in oxidizing environments.   Iron dissolved in water containing sulfide would ultimately be precipitated, unless the pH and Eh both were relatively low (fig. 7).   Oxides and hydroxides of iron might also be converted to sulfides.   Precipitation of these and other metallic sulfides probably tends to minimize the content of reduced sulfur species in ground water.

Zobell (1946) reported measurements of Eh as low as -0.50 v in certain marine muds.   Sulfate obviously would tend to be reduced in such environments.

OXIDATION OF PYRITE

Many sedimentary rocks contain some iron in the form of pyrite. This iron becomes available for solution above Eh 0.03 v at pH 4 and above Eh -0.32 v at pH 9 (fig. 7).   The relative instability of pyrite in the presence of air and water is expected from the Eh value of about 0.40 v that is typical of aerated water.   Oxidation of pyrite in soil and in water-table aquifers can be an important source of iron in ground water.

Figure 8 shows that the solubility of pyrite because of oxidation to Fe^{+2} and SO_4^{-2} increases rapidly with rising Eh at any fixed pH. For example, the boundary for $[Fe^{+2}] = 100$ ppm lies only about 0.02 v above the 0.01 ppm $[Fe^{+2}]$ line.   The rate of increase of iron at saturation with respect to the $Fe(OH)_3$ boundary as Eh decreases is much less.   Figure 8 shows that to raise the activity of iron from the detection limit to 100 ppm in a ferrous-ferric system at pH 6.0, the Eh must be lowered by 0.14 v.

The rapid increase in solubility of pyrite with an increase in Eh suggests that pyrite is likely to be relatively unstable in most groundwater environments.   If the Eh rises to the level expected in aerated water (about 0.40 v), any iron dissolved from pyrite will be redeposited as oxide or hydroxide.   Some of the phenomena associated with the occurrence of iron in ground water can be logically explained from relations shown in figure 8.

SOLUTION AND DEPOSITION OF IRON IN AQUIFERS

Erratic changes in iron content of ground water are often observed as wells are pumped.   Water from adjacent wells may differ in iron

content although their waters are similar in other chemical characteristics. The iron content may vary with time as the well is pumped, or with pumping rate. Some of these changes can be better understood with knowledge of the chemical behavior of iron in the presence of sulfur or carbon dioxide. In soils and substrata, pyrite is oxidized during weathering. The oxidation, however, is less complete as depth increases. In the zone of saturation, there may be much more stratification with respect to iron content of the water than with respect to other solutes. Near the water table, redox potentials are high—usually within the $Fe(OH)_3$ stability zone—and nearly all reduced dissolved iron that enters this zone may be deposited from solution. Where the aquifer is continuously saturated, the Eh commonly will be low enough to permit some ferrous iron to remain in solution. In some places, however, conditions might be favorable for pyrite oxidation, which would add to the dissolved-iron content of the water. At great depths or where conditions are favorable for sulfate reduction, the water will be low in iron content as a result of sulfide precipitation.

Most wells may obtain water both from oxidizing zones near the water table and from less-oxidizing zones deep in the aquifer, and the iron content of these water sources may be different. Fluctuations of the water table in heavily pumped areas cause air to replace part of the water in the dewatered zone and may render this zone much more oxidizing than normal. Ferrous iron in the residual water of this zone can be oxidized and precipitated as ferric hydroxide. The resaturation of temporarily dewatered zones tends to reimpose reducing conditions. The deposited ferric hydroxide may then be reduced and redissolved. More likely, however, it will remain as a coating on the aquifer mineral grains, and repetition of the cycle can cause a thickening of the coating.

The oxidation of iron in a developed aquifer whose water is iron bearing may have important physical effects. As air enters the aquifers when pumping wells draw the water level down, precipitates of ferric hydroxide may accumulate which are sufficient to reduce the transmissibility of part of the saturated zone.

In some aquifers containing pyrite the oxidation of pyrite may be relatively rapid within cones of depression around pumping wells and may lead to peculiar fluctuations of iron content as the pumping rate changes.

Colonies of "iron bacteria" have become established in or near wells where a transitional zone between low and high Eh exists. These bacteria accelerate oxidation and precipitation of the iron from water that passes through such a zone; the amount removed depends in part on the rate of water movement induced by pumping. Occasionally,

precipitated iron may break loose from the bacterial colony, enter the well, and be pumped out.

Although the Eh-pH relations for sulfur should be interpreted more cautiously than those of ferrous-ferric equilibria, the comments given in this report help to explain many of the features of the chemistry of iron in ground water that have perplexed water users and hydrologists.

Some of the problems associated with iron in ground water probably could be resolved if the effects discussed in this report are kept in mind. For successful utilization, an iron-bearing ground water must be recognized as an unstable chemical system.

LITERATURE CITED

Garrels, R. M., and Naeser, C. R., 1958, Equilibrium distribution of dissolved sulfur species in water at 25° C and one atmosphere total pressure: Geochim. et Cosmochim. Acta, v. 15, p. 113–130.

Hem, J. D., 1960,   Restraints on dissolved ferrous iron imposed by bicarbonate, redox potential, and pH: U.S. Geol. Survey Water-Supply Paper 1459–B, p. 33–55.

Hem, J. D., and Cropper, W. H., 1959, A survey of ferric-ferrous chemical equilibria and redox potentials: U.S. Geol. Survey Water-Supply Paper 1459–A, p. 1–31.

Huber, N. K., and Garrels, R. M., 1953, Relation of pH and oxidation potential to sedimentary iron mineral formation: Econ. Geol., v. 48, p. 337–357.

Krumbein, W. C., and Garrels, R. M., 1952, Origin and classification of chemical sediments in terms of pH and oxidation potentials: Jour. Geol., v. 60, p. 1–33.

Latimer, W. M., 1952, Oxidation potentials: New York, Prentice-Hall, 392 p.

Pourbaix, M. J. N., 1949, Thermodynamics of dilute aqueous solutions: London, Edward Arnold & Co., 136 p.

Zobell, C. E., 1946, Redox potential of marine sediments: Am. Assoc. Petroleum Geologists Bull., v. 30, p. 477–513.

○