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Stability Field Diagrams as Aids in Iron Chemistry Studies

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IRON is one of the most common and widely distributed elements in the earth's crust. It is a constituent of most rocks and soils. The chemical behavior of the element, however, generally favors its retention in minerals of low solubility. In natural water, therefore, dissolved iron is present in minor amounts, except when special chemical conditions exist. An understanding of the behavior of iron in natural water can be gained by a detailed consideration of the kind of chemical conditions that favor its solution. Such an understanding is important, because iron, even in minor amounts, is an undesirable impurity in water supplies.

For several years, research has been conducted by USGS on the chemistry of iron in natural water. A series of reports summarizing the work has been published.[1-4] The features of iron chemistry that have been studied are:

1. *Oxidation and reduction.* Iron occurs in nature in the trivalent (ferric) and divalent (ferrous) forms. The behavior of the two forms is different; the conversion of iron from one form to the other is relatively easy.
2. *Hydrolysis.* Both ferrous and ferric ions hydrolyze in solution. The form and behavior of the hydroxides are closely related to the pH of the system.
3. *Formation of compounds of low solubility.* Several anions that are commonly found in natural water, at or near the land surface, and in ground water can combine with ferrous or ferric iron to form nearly insoluble compounds. Ferrous carbonate and ferrous sulfide are important iron minerals whose solubility is related to pH.
4. *Formation of soluble complex ions.* Iron is capable of combining with certain organic ions and some inorganic ones to produce anion or cation complexes sufficiently stable and soluble to affect the transport of iron in surface water, soil moisture, and ground water.
5. *Iron in colloidal suspensions.* Particles of iron oxides or hydroxides in or near the colloidal size range may be carried with a considerable degree of stability in river water. Amounts present in this form in clear water, however, rarely exceed a few hundredths or tenths of a part per million.
6. *Biochemical factors.* Iron is an essential element in both plant and animal metabolism. Therefore, concentrations and forms of iron dissolved in natural water may often be influenced by plants and animals. The influence may take the form of catalysis, which increases the rate of a chemical reaction, or the biologic effect may involve the utilization of energy ob-

tained through a metabolic process to promote a chemical reaction involving iron.

Common iron-bearing minerals of rocks and soils include oxides, carbonates, and sulfides. Under certain conditions, any of these may be attacked by water, and enough iron may thus go into solution to be troublesome to the water user. Iron oxides, for example, are dissolved by water at a nearly neutral pH below the water table if oxygen is almost entirely absent. Under these conditions iron carbonate may also be quite soluble. The sulfide minerals containing iron, of which pyrite is probably the most common, are relatively insoluble in alkaline-reducing environments but can be dissolved easily when oxidizing conditions prevail. In the following discussion, these relationships will be considered quantitatively.

Redox Potential and Iron Behavior

The oxidation of an ion of ferrous iron is represented by:

$$Fe^{++} \rightarrow Fe^{+++} + e$$

in which e represents the electron, bearing a unit negative charge, that is released by the oxidation of the ferrous ion. In a solution containing ferrous and ferric ions, the relative proportion of oxidized and reduced forms is indicated by the effective supply of these charges. An inert metal electrode immersed in such a solution will attain an electrical potential whose magnitude depends on the ratio of ferric to ferrous ions. If a standard reference electrode is immersed in the solution, the electrical potential between it and the inert electrode can be measured. This potential is called the reduction-oxidation (redox) potential and is a measure of the relative activities of oxidized and reduced ions.

The redox potential is commonly represented by the symbol E or E_h, the h in the symbol indicating that the potential is measured with respect to the standard hydrogen electrode as zero. The standard potential, E^0, for a redox couple is the value attained when the reacting substances are present at unit effective concentration or activity. Whether the potential is considered negative or positive, however, is an arbitrary matter. Standard practice in electrochemistry is to consider increasing oxidizing potentials as increasing positive values. This general practice has been followed in applications of E_h in water chemistry, geochemistry, and biochemistry.

The free energy of a chemical substance, generally expressed in kilocalories, is the energy available from that material when the temperature remains constant. The standard free energy of formation of a chemical compound, a value commonly used in thermodynamic calculations, is the change in free energy that occurs when one formula weight (in grams) of the compound is formed from the elements at standard states (temperature 25°C and pressure 1 atmosphere). The net change in standard free energy in a chemical reaction is the difference between the total free energy of formation of the products and that of the initial substances. Free-energy values are useful indexes of chemical behavior.

Fundamental equations of chemical thermodynamics interrelate the standard free-energy change resulting from a chemical reaction, the equilibrium constant for the reaction, the amounts of the reacting substances present at equilibrium, the standard potential, and the redox potential. The equations are:

$$\Delta F^0 = - RT \log_e K \ldots\ldots\ldots (1)$$

$$E^0 = - \frac{\Delta F^0}{nf} \ldots\ldots\ldots\ldots (2)$$

$$E_h = E^0 + \frac{RT}{nf} \log_e \frac{a_{ox.}}{a_{red.}} \ldots\ldots\ldots (3)$$

in which ΔF^0 is the standard free-energy change in the chemical reaction (in kilocalories); R, universal gas constant (1.987 calories per degree per mole, or 8.314 joules per degree per mole); T, absolute temperature; n, number of electrons, represented by a multiple of e in the redox equation; f, Faraday constant (23,060 calories/volt, or 96,484 coulombs/gram equivalent); E^0, standard potential (in volts); E_h, redox potential; and $a_{ox.}$ and $a_{red.}$, effective concentrations of oxidized and reduced substances in the chemical system being considered. If oxidizing potentials are to be considered positive, these equations will give correct values for equilibrium conditions when the reactions are written as reductions—that is, when e appears on the left side of the chemical equation.

In many published articles dealing with relations of E_h and pH in chemical equilibria in natural water, the reactions have been written as oxidations, with e appearing on the right side of the expression. If this is done and oxidizing potentials are still to be considered positive, it is necessary to change the sign of E^0 either in Eq 2 or Eq 3. Pourbaix,[5] who pioneered the use of thermodynamics in studies of metallic corrosion and developed the stability field diagram, followed this procedure, and later writers[6] used the same procedures as those of Pourbaix. The author also has used Pourbaix's technique in describing the relationships among E_h, pH, and iron content of natural water.[2,3] To be consistent in this article, redox reactions are written as oxidations, and the sign of E^0 in Eq 2 is changed.

The substitution of appropriate constants in Eq 1–3 and a change to logarithms to the base 10 give, at 25°C:

$$\Delta F^0 = - 1.364 \log K \ldots\ldots\ldots (4)$$

$$E^0 = \frac{\Delta F^0}{(23.06)\, n} \ldots\ldots\ldots\ldots (5)$$

$$E_h = E^0 + \frac{0.0592}{n} \times \log \frac{a_{ox.}}{a_{red.}} \ldots\ldots (6)$$

The E_h of a solution can be measured by means of a sensitive potentiometer or electrometer, such as a pH meter, connected to a platinum or other inert-metal electrode and a standard electrode immersed in the solution.

Measurement of E_h

Laboratory experiments[1] have shown that values of E_h measured in solutions in the laboratory agree reasonably well with values computed from pH measurements and iron concentrations in these solutions. Agreement of the computed E_h with measured E_h for ground water, however, has not been fully ascertained. The techniques for measurement of E_h in ground water are still in a rather early stage of development. The effect of oxygen from the air is generally the dominant factor in establishing the E_h of a natural water at or near the land surface. The large supply of oxygen available for solution as a result of the contact between air and water exerts a stabilizing effect on the E_h of the solution analogous to the stabilizing of pH by the action of a buffer system. In E_h measurement, the stabilizing effect is

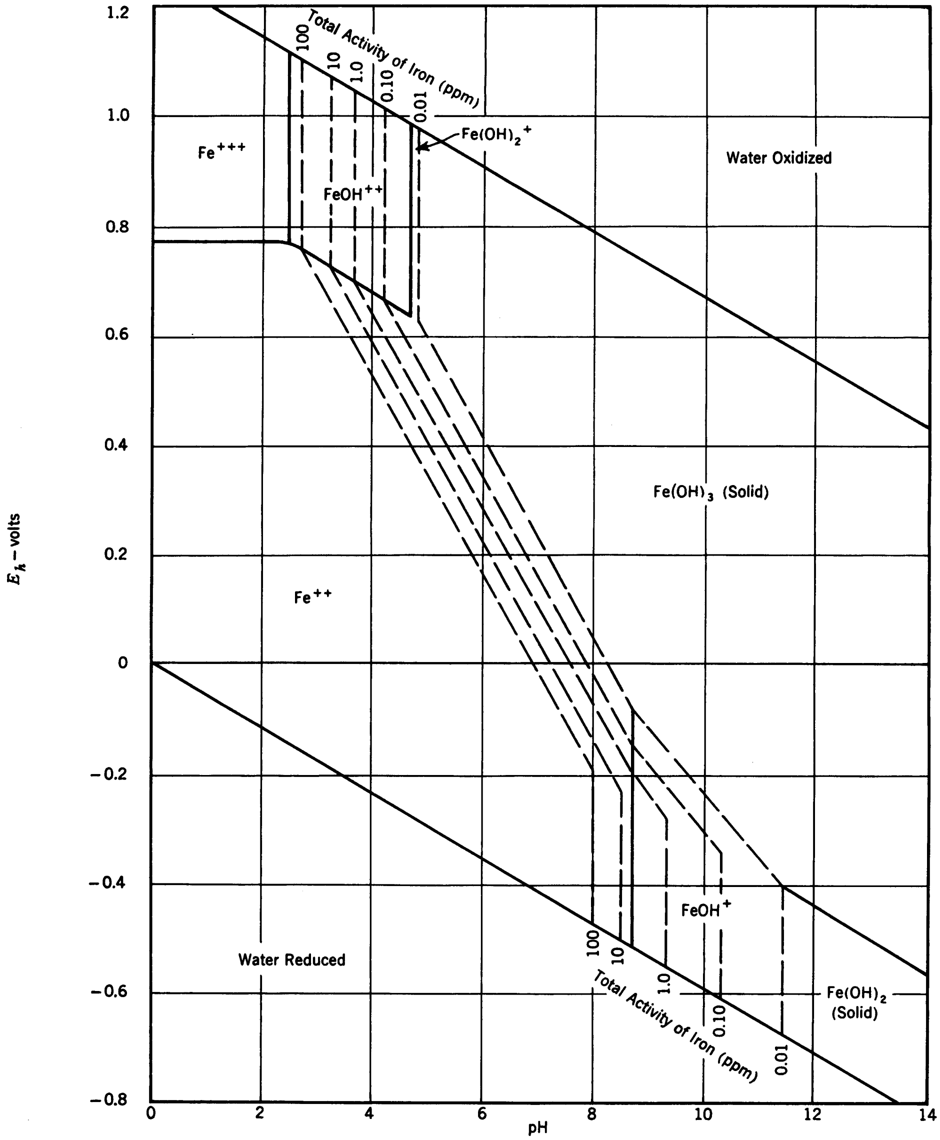

Fig. 1. Stability Fields of Ferrous and Ferric Species for Activities of 0.01–100 ppm Dissolved Iron

The upper sloping boundary represents the potential at which water is broken down by oxidation to form oxygen gas and hydrogen ions. The lower sloping boundary represents the potential at which water is broken down by reduction to form hydroxyl ions and hydrogen gas.

termed "poising." In ground water, poising effects can occur from solids that are in contact with the water. When the water is removed from the aquifer, the poising effect is diminished, because the E_h then depends only on dissolved ions that are usually present in minor amounts. The E_h then can be easily changed by introducing a new factor, such as small amounts of atmospheric oxygen. The E_h of a ground water may thus be changed during the process of pumping the water to the land surface. Some degree of E_h stratification within aquifers also could occur, the higher values occurring near the top of the water-saturated zone where some contact with air may occur.

A probing device containing E_h and pH electrodes, which does not introduce air where it is inserted, is needed for measurement of E_h in unconfined ground water. Such devices have been used for measurements in open water bodies by limnologists, and one was developed and used by the author in studies of the effects of aquatic vegetation on the iron content of water.[7] Probes have also been used for measurement of E_h in soil.[8]

Weart and Margrave[9] made measurements of E_h in water in studies of the performance of iron removal plants in Illinois. They found the measurements helpful in evaluating the efficiency of iron removal.

Since 1955, USGS has conducted experiments with methods of measuring E_h in the field, in connection with studies of the occurrence of uranium in ground water. The results of several hundred such measurements have shown that water from pumped wells usually has been affected by atmospheric oxygen by the time the water has reached the land surface where the E_h electrodes of conventional measuring equipment can be inserted in the pump discharge. A similar effect generally occurs in springs. But some measurements of E_h made by inserting the electrodes into the discharge pipe of flowing artesian wells appear to be free from the effects of oxygen.

Studies of methods of field measurement of E_h in ground water reported by Germanov and others[10] parallel the findings of USGS. The development of measuring techniques is continuing. Water in contact with the atmosphere generally has an E_h of +0.35 to 0.50 v at a nearly neutral pH.

Preparation and Use of Diagrams

The stability field diagram is a graph on which pH is plotted as the abscissa and E_h as the ordinate. The chemical system to which the diagram applies generally involves one or more solid compounds of known chemical composition in contact with water at a stated pressure and temperature. A pressure of 1 atmosphere and a temperature of 25°C are the standard conditions used. Boundaries of areas on the diagram in which particular species of ions or solids would be stable at chemical equilibrium can be computed for given concentrations of dissolved ions with the use of the equations given before.

Work by Hem and Cropper[1] showed that most hydrolysis or oxidation reactions involving iron are rapid enough for equilibrium to be attained in many natural waters, except at low pH. The departure from standard conditions of temperature and pressure in many such systems is not great enough to affect the position of the stability boundaries much. Thus, the stability field diagram is of considerable practical value in studies of the chemistry of iron in water. Pourbaix,[5] who apparently originated the graphic procedure, has applied it extensively in his study of corrosion of metals. For example, a region of stability for metallic iron can be defined, and corrosion will not occur if E_h and pH remain at values within the field of stability for iron. During the past few years, geochemists and biochemists have used stability field diagrams rather extensively. The work of Garrels[11] is particularly noteworthy. It should be emphasized, however, that the diagram cannot be used for predicting reaction rates.

Figure 1 is a simple stability field diagram for a solution of iron in distilled water in contact with ferric hydroxide or ferrous hydroxide. Ferric hydroxide may also be considered to be hydrated ferric oxide, $Fe_2O_3 \cdot 3H_2O$. The upper sloping boundary on the diagram represents the potential at which water would be broken down by oxidation to form oxygen gas and hydrogen ions:

$$2H_2O \rightleftharpoons O_2 + 4H^+ + 4e.$$

The lower sloping boundary represents the potential at which water would be broken down by reduction to form hydroxyl ions and hydrogen gas:

$$2H_2O + 2e \rightleftharpoons H_2 + 2OH^-.$$

The locations of the water stability boundaries are determined from values for the standard potential E^0 for these two reactions and Eq 6. The standard potentials are readily available in the literature[11] or can be computed from free-energy data and Eq 5. The activities of water and the gases are unity by definition. Thus, for the oxidation reaction, Eq 6 becomes:

$$E_h = 1.23 + \frac{0.059}{4} \log [H]^4$$

$$= 1.23 - 0.059 \text{ pH}.$$

For the reduction reaction, Eq 6 becomes:

$$E_h = -0.83 + 0.059 (14 - \text{pH}).$$

At equilibrium, any water solution will have E_h and pH values within the limits of the water stability boundaries. Because of overvoltage effects and slowness of some reactions, however, redox potentials outside the limits can be observed. The next step in preparing Fig. 1 was to determine the positions of boundaries separating ferric species where the E_h is high enough to prevent any reduction from taking place.

Relative to this discussion, the hydrolysis reactions involving ferric ions in distilled water are:

$$Fe^{+++} + H_2O \rightleftharpoons FeOH^{++} + H^+$$

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

$$Fe(OH)_2^+ + H_2O \rightleftharpoons Fe(OH)_3\,c + H^+.$$

The symbol c following a chemical formula means that the substance is present in the crystalline or solid state.

Similar reactions could be written for the various ferrous species. If the redox potential is high or low enough so that the iron is essentially all present either in the ferric or ferrous form, the species of ion that will predominate is a function of pH alone. Data in the literature relating to these reactions have been collected.[1] Equilibrium (hydrolysis) constants for these reactions can be taken directly from published values or can be computed from standard free-energy data as given by Latimer[12] and the expression:

$$\Delta F^0 = -1.364 \log K.$$

The vertical boundaries are obtained by computing the pH at which the ratio of the activities of the two species separated by the boundary has a value of unity. For example, in the first hydrolysis equilibrium, the expression for the hydrolysis constant K_h is shown to be:

$$K_h = \frac{[FeOH^{++}][H^+]}{[H_2O][Fe^{+++}]}.$$

The water is present at unit activity. Hence, all the activity terms except [H] cancel out, and the pH for the Fe^{+++}–$FeOH^{++}$ boundary is:

$$pH = -\log K_h$$

which, for this equilibrium, has a value of 2.4. Similar computations give pH values for boundaries separating the other hydroxides of ferric and ferrous iron.

The position of the boundary of stability for the two solids ferric and ferrous hydroxide depends on the value chosen for the limit of iron solubility. Activities of solids are taken as unity. Five different boundaries for stability of solids are given as dashed lines in Fig. 1. The one giving the smallest area for stability of the solids is based on a dissolved-iron activity of 0.01 ppm, the lower limit of detection by the 2,2′-bipyridine method as it is usually applied in water analysis. An activity of iron of 1.8×10^{-7} molal is equivalent to 0.01 ppm. Other boundaries are drawn for dissolved-iron activities of 0.10 ppm, 1.0 ppm, 10 ppm, and 100 ppm. Solid lines are boundaries separating dissolved species or different solid compounds and are independent of iron concentration. The position of the stability boundaries of solids depends also on the crystal form and purity of the solid.

The boundaries separating the ferric from the ferrous species are determined from the equilibria:

$$Fe^{++} \rightleftharpoons Fe^{+++} + e$$

$$Fe^{++} + H_2O \rightleftharpoons FeOH^{++} + H^+ + e$$

$$Fe^{++} + 2H_2O \rightleftharpoons Fe(OH)_2{}^+ + 2H^+ + e$$

$$Fe^{++} + 3H_2O \rightleftharpoons Fe(OH)_3\,c + 3H^+ + e$$

$$FeOH^+ + 2H_2O \rightleftharpoons Fe(OH)_3\,c + 2H^+ + e$$

$$Fe(OH)_2\,c + H_2O \rightleftharpoons Fe(OH)_3\,c + H^+ + e.$$

The values of E^0 for the equilibria can be computed from free-energy data compiled by Hem and Cropper[1] and from Eq 5. E_h values can then be computed from Eq 6. In this computation, the ratios of ferric to ferrous species are taken as unity, except where one or more are present as a solid. When this condition exists, the activity of the solid is taken as unity, and the computation is made by entering in the equation a selected value for the activity of dissolved iron (0.01 ppm, 0.10 ppm, 1.0 ppm, 10 ppm, or 100 ppm). The boundary between the two solids is independent of dissolved-iron activity. For example, in the equilibrium:

$$Fe^{++} + H_2O \rightleftharpoons FeOH^{++} + H^+ + e$$

ΔF^0 equals 21.08 kilocalories. From Eq 5:

$$E^0 = \frac{21.08}{23.06} = 0.91 \text{ volts.}$$

After substitution in Eq 6:

$$E_h = 0.91 + \frac{0.059}{1} \log \frac{[FeOH^{++}][H^+]}{[Fe^{++}]}.$$

This reduces to:

$$E_h = 0.91 - 0.059\ pH$$

when the ratio of the two iron species is unity. The result of the calculation of the ferrous-ferric boundary is a

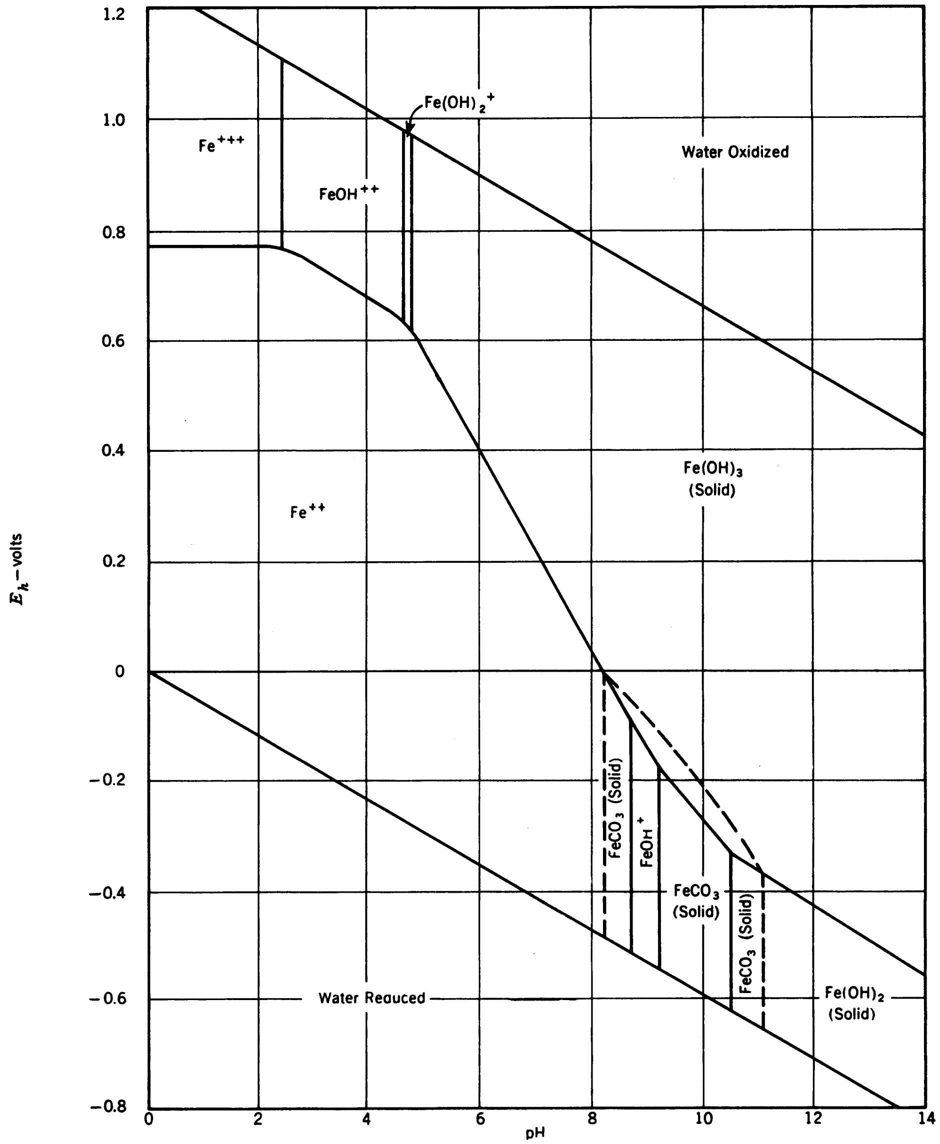

Fig. 2. Stability Fields of Ferrous and Ferric Species for Activity of 0.01 ppm Dissolved Iron

The system contains carbonate species activity equivalent to 100 ppm as bicarbonate (solid boundaries) or 1,000 ppm as bicarbonate (dashed boundaries).

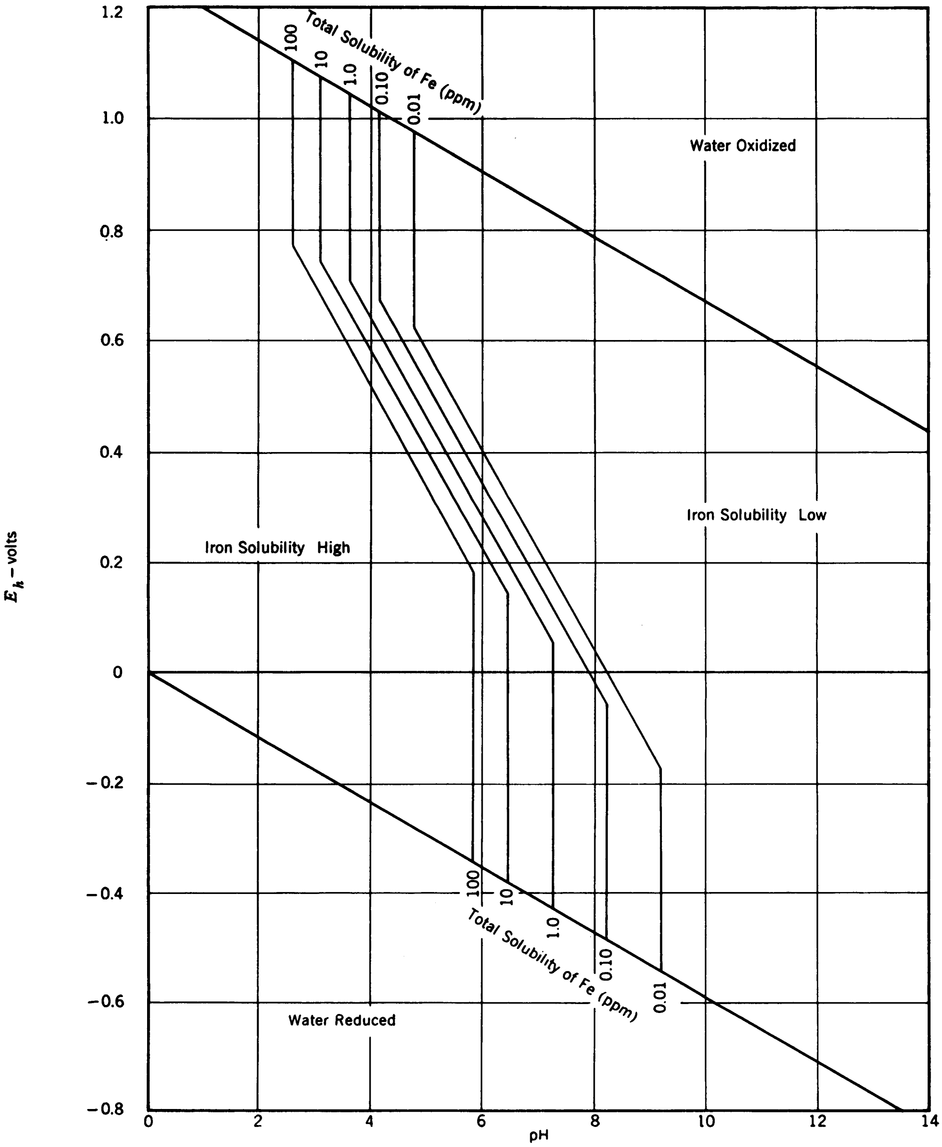

Fig. 3. Solubility of Iron in Relation to pH and E_h

The carbonate species activity was equivalent to 100 ppm as bicarbonate. Bicarbonate activity equivalent to 100 ppm or more is common in ground water.

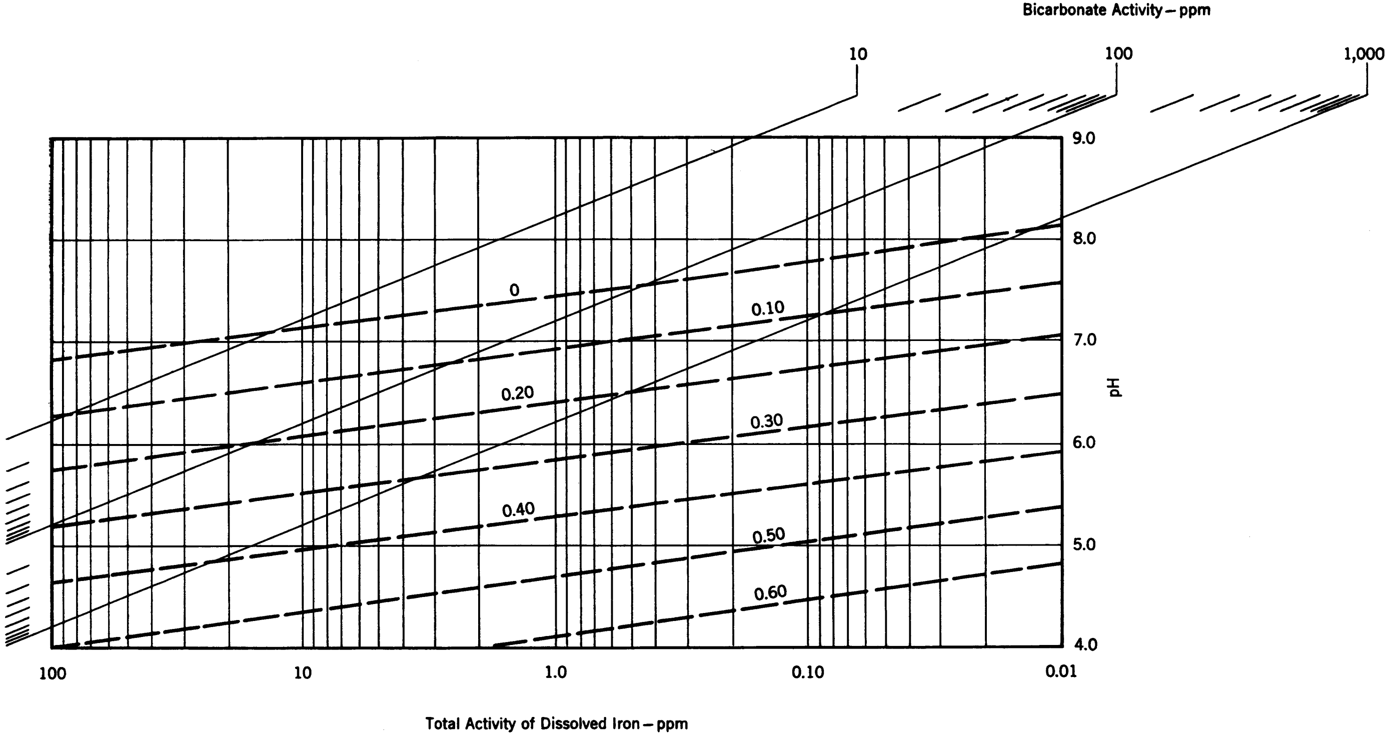

Fig. 4. Relationships of Dissolved Iron, pH, E_h, and Bicarbonate Activity

The values on the dashed curves are E_h *values. The figure represents a means of estimating* E_h *of iron-bearing ground water in its native environment.*

curve whose slope changes as it passes each of the vertical boundaries, and the form of ions or solids changes.

The stability field diagram may be applied in several ways. If the particular interest is in the solid substance involved, as in corrosion problems, the diagram will show the conditions that will minimize the attack of the solvent on the solid. In studies of water chemistry, the diagram is an aid in showing factors that affect the solubility of iron. Figure 1 can be used as a solubility diagram that depicts the correlations among E_h, pH, and iron content in a distilled-water system.

The relationships shown in Fig. 1 do not take into account certain important factors that are usually involved in natural waters. For example, if some carbon dioxide is present in solution, the presence of another solid, ferrous carbonate, will be possible and must be considered as a possible control over the solubility of iron. Solid lines in Fig. 2 represent a system containing dissolved-carbonate species, equivalent to an activity of 100 ppm in terms of bicarbonate ions, and an activity of 0.01 ppm of iron. The size of the stability region for $FeOH^+$ in Fig. 2 is much smaller than that in Fig. 1. The dashed lines in Fig. 2 show the effect of an activity of dissolved-carbonate species of 1,000 ppm in terms of bicarbonate ions. This eliminates the $FeOH^+$ field entirely. Ferrous carbonate, however, will be oxidized to ferric oxide at the E_h of aerated water; hence, it is important only in anaerobic environments.

The position of the $FeCO_3$–Fe^{++} boundary is computed from the equilibrium:

$$FeCO_3 + H^+ \rightleftharpoons Fe^{++} + HCO_3^-$$

and the relationship of the standard free-energy change to the equilibrium constant.

A three-dimensional graph could be made in which pH, E_h, and activity of carbonate species are plotted to show the effect of bicarbonate and related species over a considerable concentration range. Figure 2 represents only two bicarbonate values. Figure 3 shows the solubility of iron in water in the presence of dissolved-carbonate species in amounts equivalent to an activity of 100 ppm as bicarbonate. The figure shows that even this moderate amount of bicarbonate greatly decreases the solubility of iron at low redox potentials. Bicarbonate activity equivalent to 100 ppm or more is common in ground water.

The carbonate species considered in Fig. 2 and 3 include not only carbonate and bicarbonate ions but also undissociated carbonic acid and dissolved carbon dioxide. The undissociated forms constitute an increasingly important part of the total as the pH decreases to less than 7.

E_h of Ground Water

The relationships among pH, iron content, E_h, and bicarbonate activity are expressed in somewhat different form in Fig. 4. In the figure, iron activities are plotted as the abscissa; pH, as the ordinate. A grid of E_h curves is superimposed by the use of computations the same as were made for Fig. 1.

Figure 4 represents a means of estimating E_h of iron-bearing ground water in its native environment. The estimate can be made for any water for which there can be obtained a pH value that represents accurately the actual pH in the aquifer and which is free from suspended iron at the time of sampling. In the absence of interfering ions, the iron activity for use in the E_h estimates can be obtained from the total amount of iron reported in the sample, including any iron that precipitated in the sample bottle after collection. The pH and iron values result in a point on Fig. 4 whose relationship to the E_h grid represents the E_h of the water. The figure was developed by the author during his studies of iron chemistry.[2]

An important limitation on the use of Fig. 4 is the effect of bicarbonate. In those solutions in which the bicarbonate activity is high enough to precipitate ferrous carbonate, a decrease in E_h may not have any effect in bringing more iron into solution. The curves in Fig. 3 denoting iron content are vertical in the region where iron solubility is affected by carbonate precipitation, showing that iron content is not E_h-dependent in this region. They are also vertical in the ferric region at low pH, but these conditions are not included in Fig. 4.

When Fig. 4 is used for estimating E_h, the bicarbonate activity in the solution should first be ascertained. A straight line can then be projected on the figure for the bicarbonate activity value, with the bicarbonate activity scale at the top of the diagram. The pH–iron activity intersection should then be ascertained. If this point is below the bicarbonate line for the water, the E_h can be estimated from the position of the point with respect to the E_h grid. If, however, the pH–iron activity intersection lies on the bicarbonate line or above it, the system probably is under the influence of ferrous carbonate, and an E_h estimate cannot be made. The formation of complex ions may also interfere with the use of the figure.

The difficulties of measuring E_h have been pointed out. A knowledge of the E_h in aquifers, however, is essential for studying some features of natural-water chemistry. For example, the chemical compatibility of water proposed for underground injection with water already in the formation can be predicted more readily if the E_h can be estimated. This kind of problem can be expected to occur with increasing frequency in studies of ground water recharge or pollution, or the use of deep salt water aquifers for waste disposal. In those systems for which an estimate of E_h can be made from analytic data, the method should be of practical value, even though it has limitations.

The results obtained in E_h estimates depend on the obtaining of meaningful pH determinations. The pH value obtained in the laboratory after the sample has been stored for several days or weeks and has been opened a few times, perhaps to take out portions for various chemical determinations, may have little relationship to the pH value that the water had in the aquifer underground. The only pH values that are useful in E_h estimates are those that represent the water in its natural surroundings. The pH determinations must be made in the field immediately after the water has issued from the well or spring. Some waters may change in pH even before the field determination can be made, but this degree of instability is probably unusual.

The pH measurement should be made with a method that is accurate to a pH unit of 0.1. Test paper or other devices for making pH approximations are not suitable for this purpose. The temperature of the water should be within 10–15 deg of 25°C if Fig. 4 is to be used with reasonable accuracy.

Complex-Ion Formation

The discussion of pH-E_h-iron relationships thus far has assumed that chemical equilibrium has been established. In some natural waters, this is not a completely safe assumption. Ferrous and ferric iron form complex ions with some organic materials that may be found in soils or the leach from organic debris. The complexed iron is still subject to oxidation, but the reaction rate may be changed. Also, the E_h at equilibrium may be different from the value attained with uncomplexed iron. The author has investigated a complex involving ferrous iron and tannic acid which has an oxidation half-life in contact with air of approximately 30 days at pH values near 8.0.[3] This compares with a half-life of a few minutes for the oxidation of uncomplexed ferrous ions at this pH. Soluble complexes of ferric iron with organic matter are common. Inorganic ions such as phosphate also form ferric complexes. Also, there may be some complexing between bicarbonate and ferrous ions, but this has not been definitely ascertained. In any event, E_h-pH-iron relationships may require special study where complexing occurs. Natural water that has a noticeable color may contain complexed iron and may not yield useful data for E_h estimates.

Colloidal Ferric Hydroxide

Water may contain relatively stable colloidal suspensions of ferric hydroxide.[1] Much of the iron in clarified surface waters appears to be in this form, but the amount present generally is only a few hundredths of a part per million. The effects of colloidal iron may distort the analytic data for dissolved iron when the amount present is less than approximately 0.10 ppm. Hence, the relationships among iron, E_h, and pH may not be well defined at this concentration.

Effective and Measured Concentrations

Throughout this article, thermodynamic effective concentration or activity values are used instead of the measured concentrations obtained in water analyses. The activities of ions in dilute solutions are always somewhat less than the actual concentration present, because of interionic forces, combination with molecules of the solvent, and other effects. As total concentrations in natural waters increase, the difference between activities and measured concentrations increases also, at least up to a concentration near 5,000 ppm dissolved solids.

Methods for computing activities from concentrations are given by Klotz,[13] and some applications of these techniques to natural waters have been described by the author.[2] In waters whose concentration of dissolved solids is less than approximately 100 ppm, activities and measured concentrations will generally differ by not more than 10–15 per cent. At concentrations of approximately 1,000 ppm, however, activities of such divalent ions as Fe^{++} may be only half as great as the measured concentration values. For most waters, therefore, activity corrections of the measured concentrations are necessary to give satisfactory accuracy in calculated relationships. Measured pH values, of course, are themselves effective hydrogen ion con-

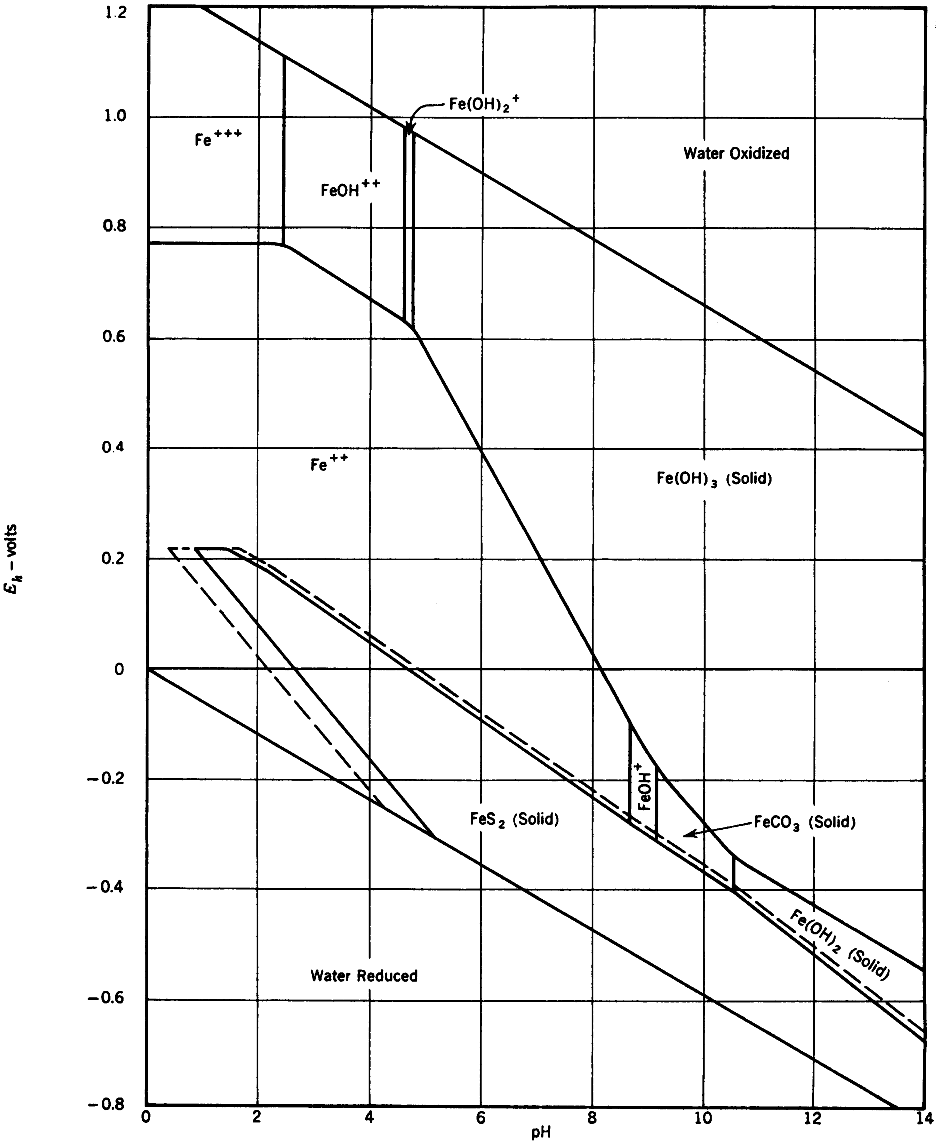

Fig. 5. Stability Fields of Ferrous and Ferric Species for Activities of 0.01 ppm Dissolved Iron and 100 ppm Carbonate Species as Bicarbonate

The system contains sulfur equivalent to 10 ppm as sulfate (solid boundaries) or 100 ppm as sulfate (dashed boundaries).

centrations, and they require no correction.

Dissolved-Sulfur Species

Sulfur is susceptible to oxidation or reduction and can exist in many forms, ranging from S^{--}, as in sulfide, to S^{6+}, as in sulfate. Thermodynamic calculations show, however, that few of these forms would be stable in natural water. A stability field diagram for sulfur can be prepared showing the forms that would be expected in water.[6] The effects of sulfur species in solution in a system that also contains iron and bicarbonate have been described in a previous study.[4] Figure 5 is a representation of such a system.

Oxidation and reduction reactions of sulfur unfortunately are not ideal subjects for representation in stability field diagrams. The equilibrium condition assumed for the preparation of these diagrams often is not attained in natural waters containing sulfate or other dissolved forms of sulfur.

The solid lines in Fig. 5 represent a system containing activities of 0.01 ppm iron, 100 pm dissolved-carbonate species as HCO_3^-, and 10 ppm dissolved-sulfur species as SO_4^{--}. The extent of the pyrite field when the sum of the sulfur species is 100 ppm as sulfate is indicated by dashed lines. The close spacing of the iron solubility lines along the top of the pyrite field shows that a minor increase in E_h could have marked effects. The solution of pyrite in this region involves oxidation of sulfur from S_2^{--} to SO_4^{--}.

Figure 6 is a solubility diagram for iron in a system at equilibrium containing a total dissolved-carbonate species of 100 ppm as HCO_3^- and a total dissolved-sulfur species of 10 ppm as SO_4^{--}. Water may retain sulfate for a very long time, even though it is subjected to E_h and pH conditions within the field of stability of FeS_2.

Bacterial Action

The effects of bacterial action on the behavior of iron are important in a number of respects. Bacteria, however, cannot produce results that are contrary to the laws of thermodynamics. They can promote such reactions as sulfate reduction, which requires an outside supply of energy, only when they are able to obtain energy from sunlight or from the breakdown of compounds that yield energy, such as in the oxidation of hydrocarbons. Bacterial action will go on if the E_h and pH of the environment are favorable for the continued existence of the bacteria. Therefore, the stability field diagrams presented here are applicable whether bacteria are present or not. The bacteria may change the rate of the reactions that would normally occur as predicted by the diagrams.

Application of Diagrams to Systems

The stability field diagrams and solubility diagrams are applicable to chemical systems that are in a state of equilibrium. In natural water in the zone of circulation in the outer part of the earth's crust, there is continual movement of water and solutes over the surface and into and out of the soil and rock materials below the surface. As a result, the pH, E_h, and dissolved-mineral content of water may change with time. Solubility diagrams, such as Fig. 3 and 6, are as applicable to a system in which water is in motion as to one in which water is at rest, if equilibrium is attained.

Solutions that have reached equilibrium with one kind of solids may be

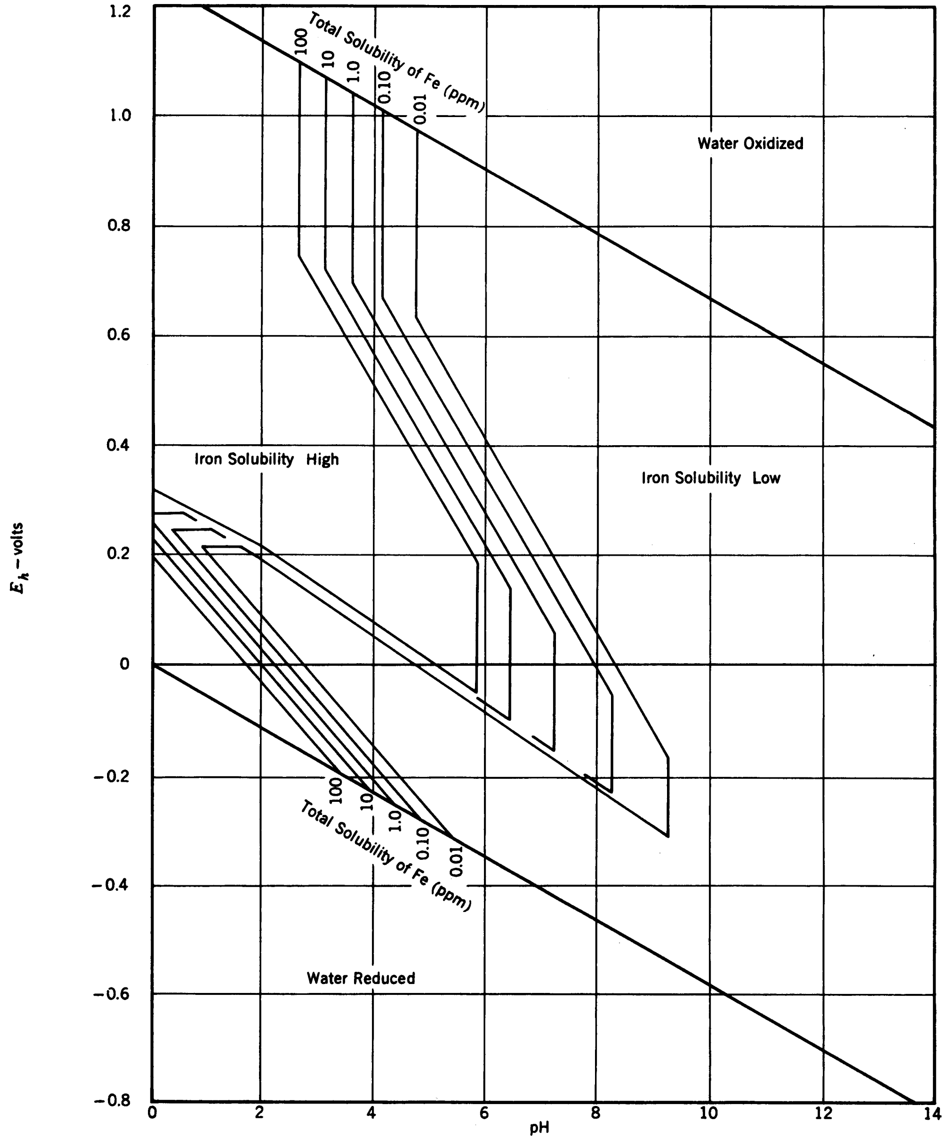

Fig. 6. Solubility of Iron in Relation to pH and E_h in a System at Equilibrium

The system contains carbonate species activity at 100 ppm as bicarbonate, and sulfur species activity at 10 ppm as sulfate.

transported into an area where the solids are entirely different, and a new set of conditions will result in changes in the composition of the solution. The E_h and pH of the solution in contact with the solid materials at a single point may change from time to time owing to the rise and fall of ground water levels and the seasonal changes of streamflow, availability of organic matter, and other factors.

Water in contact with air will have an E_h of approximately 0.35–0.50 volt, and usually its pH is greater than 5. In most of the areas relating to this condition in all the stability field diagrams, ferric hydroxide or ferric oxide is the stable form, and iron solubility is low. If the oxide is subjected to reducing conditions, however, it may be altered to give a solution containing appreciable amounts of Fe^{++}. Continued alteration will ultimately remove all the oxide, as water capable of dissolving it passes through the system and carries off the dissolved iron. The conditions could be reversed, however, by a lowering of the water table and the introduction of air, so that the dissolved iron will be redeposited in its original location or elsewhere.

Where sulfate reduction occurs, iron would be deposited as sulfide. If an iron-bearing water enters an environment in which sulfate reduction can take place, the dissolved-iron content of the moving water could easily become less than 0.01 ppm. If a pyrite deposit were subjected to oxidation, however, the close spacing of iron solubility curves, as in Fig. 6, suggests that rather large amounts of iron may be dissolved, as the difference between high and low solubility of iron at any pH is only a few hundredths of a volt in E_h. Actually, it is well known that pyrite can be readily oxidized in air when water is present and that pyrite oxidation is an important source of dissolved iron in some waters.

The numerous factors that may influence the capacity of a ground water to dissolve iron, and the ease with which some of the factors may change as water moves through the ground or as the water table rises and falls, help to explain logically some of the apparently erratic differences in iron content among similar wells and the fluctuations in iron content that sometimes occur when a well is pumped for long periods. As more information is obtained on the E_h of natural water, field evidence will become available to help show the relationships of iron and other constituents of water to the redox potential of the environment. Because such evidence is largely lacking at present, laboratory and theoretic approaches are required.

Summary

In many natural waters, the solubility of iron is controlled by the redox potential, pH, and concentrations of carbonate and sulfur anionic species. These factors can be summarized by means of stability field diagrams, which are graphs having E_h as the ordinate and pH as the abscissa. In the absence of chemical complexing and excessive amounts of carbonate, the pH and iron content of a ground water may serve as an index of the redox potential of the water in its natural environment.

Areas of stability shown on the graphs for the different ionic or solid species of iron are located by computations with the use of standard free-energy values selected from published literature. The stability field diagrams summarize the conditions required for stability of solutions containing 0.01–100 ppm iron, and indicate some factors that control solution and precipitation of iron in natural water.

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Discussion

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The author has performed a valuable service in presenting stability field diagrams as aids for the interpretation of the chemistry of iron in natural waters. The adage that one picture is worth a thousand words is pertinent to the value of redox potential–pH diagrams. Such diagrams can quickly show how hydrogen ions and electrons simultaneously shift the various iron equilibria with varying conditions, and can indicate which species predominate under any given conditions. In the opinion of the writer, graphical methods, especially in water chemistry, can be used to much better advantage than is now realized.

A potential–pH diagram is theoretical. Naturally it contains only that information used in its construction (free-energy data for the species considered). Consequently, it presents, in most instances, an oversimplified picture, but one that leads to predictions that are generally in accord with observed behavior. The value of the diagram thus consists primarily in providing an aid for the interpretation of observed facts.

E_h Measurements in Natural Media

The object of this discussion is to caution against the indiscriminate use of E_h measurements in natural waters and to discuss some of the difficulties that, in addition to those already mentioned by Hem, should be considered in the evaluation of E_h readings. As E_h measurements can be accomplished by seemingly simple techniques, it is very tempting to use such procedures for the investigation of reduction and oxidation conditions in natural waters. One would expect that such measurements would relate, in a comprensive manner, the total oxidation or reduction intensity of a natural medium. But extensive measurements of reduction-oxidation (redox) potential in surface and ground waters and in benthal deposits have, in the writer's opinion, failed to yield results that are amenable to unambiguous interpretation. It is realized that such measurements are of great value in simple systems for which the variables are known and under control, and where equilibrium conditions are established at the electrode surface. In natural waters, these criteria are not fulfilled. Such systems are complex and involve numerous reacting components—for example, various soluble iron ions and iron complexes, dissolved oxygen, different organic redox systems, and sulfides. Few, if any, of these components are known or controlled.

Complexity of Ferrous-Ferric System

The ferrous-ferric system is generally used as the standard textbook example for introducing the concept of redox potential and for illustrating the significance of the Nernst equation. The system is so complicated, however, that anyone who attempts to verify this equation by measuring E_h in a ferrous-ferric solution soon becomes frustrated by the significant discrepancy between observed and calculated data. Numerous explanations for this discrepancy can be given. The limited solubility of ferrous and ferric iron is one important consideration. Figure 7 gives the solubilities of ferrous and ferric iron in a water containing bicarbonate. As Hem and others [1-3] have pointed out, soluble iron does not exist only as Fe^{++} and Fe^{+++} ions, but consists also of various iron-hydroxo complexes such as $FeOH^+$, $Fe(OH)_3^-$, $FeOH^{++}$, $Fe(OH)_2^+$, $Fe(OH)_4^-$, and $Fe(OH)_3$ (*d*).* Figure 7, which illustrates the equilibrium relations of some of these species, is still an oversimplification, for it does not consider such soluble polymeric species as $Fe_2(OH)_2^{4+}$ and other soluble complexes that are generally present in natural waters (such as chloro-, sulfato- and phosphato-complexes). In acid solutions, in which aqueous iron is quite soluble, "formal potentials" that have been empirically determined for the given experimental conditions must be utilized.[5] The foregoing remarks do not imply that Nernst's law is not rigorously fulfilled, but they should serve to indicate that inadequate knowledge of the actual participating species may impair the proper interpretation of E_h readings.

Redox Couples in Same System

Although redox potentials in natural waters are quite frequently related to the iron concentrations, one must not overlook the fact that numerous other reactive redox components, which are not necessarily in equilibrium with one another, may be present in natural media. It is not always possible to

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* $Fe(OH)_3$ (*d*) is dissolved molecular undissociated ferric hydroxide that is believed to be in equilibrium with solid $Fe(OH)_3$.[4]

establish rigorously which of these reacting components determines or influences the measured E_h. The presence of oxygen is certainly a dominant factor in the relative "oxidation intensity" of a water. In a system where the redox potential is solely determined by the oxygen tension, a reduction in O_2 concentration from 10 mg/l to 0.1 mg/l will lower the potential by only 30 millivolts. Furthermore, the O_2-OH^- couple behaves irreversibly at a platinum electrode and thus does not give E_h values in accord with thermochemical calculations. An irreversible reaction is one in which the interchange of electrons among the electrode and the oxidized and reduced forms of the redox couple involved proceeds very slowly. Most organic redox systems behave irreversibly. Similarly, a bright platinum electrode also does not respond "properly" to the sulfide-sulfur-sulfate system.

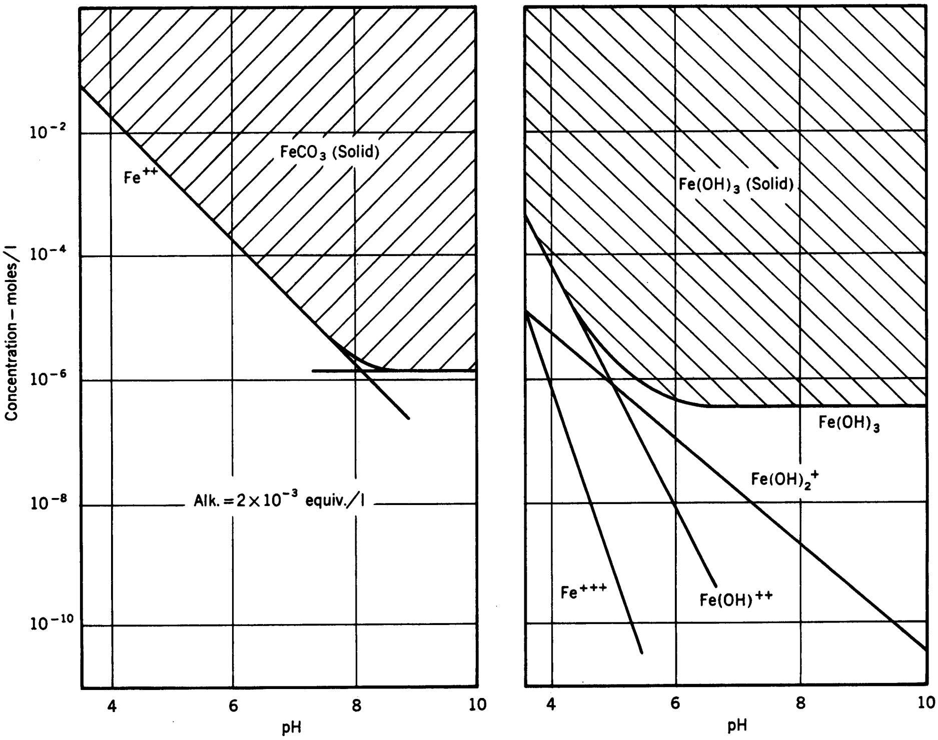

Fig. 7. Solubility of Ferrous and Ferric Iron

Left: maximum soluble ferrous iron (Fe^{++} *and* $FeOH^+$) *in a natural water containing 100 mg/l alkalinity* (*as* $CaCO_3$). *Right: maximum soluble ferric iron* (Fe^{+++}, $FeOH^{++}$, $Fe(OH)_2^+$, *and* $Fe(OH)_3$ (d).

It is highly questionable whether E_h should be listed as a factor in bacterial growth.[6] Certainly some organisms will not grow when there are too many reducing materials present, and some will not grow if there is too much oxidizing material. But the question of which factor is cause and which is effect has not been clearly answered.[6] A reversible couple, if present together with an irreversible one, can act as an electron-transfer catalyst (mediator) for the irreversible couple. Thus, the dominant role that oxygen plays in establishing the E_h of a natural water is an indirect one, and it appears likely that the reversible ferrous-ferric couple is frequently the potential-determining couple. On the other hand, the ferrous-ferric couple does not always reach equilibrium with oxygen. At low pH, ferrous iron (although thermodynamically unstable) may persist in the presence of oxygen for extensive periods of time. Figure 8 summarizes some of the results obtained by Stumm and Lee[7] on the oxygenation rate of ferrous iron in an air-saturated solution. In addition to ferrous-ferric and O_2-OH^-, other reversible and irreversible redox couples may be present in natural media: NO_3^--NO_2^-, NO_2^--NH_3, sulfide-sulfur-sulfate, and Mn^{++}-MnO_2. It is thus generally not possible to relate unambiguously the measured potential to the composition of the solution.

Apparent Potentials

E_h measurements in unpoised systems such as natural waters are not simple from a technical point of view, and extreme precaution is necessary in order to obtain reproducible readings. The response of the electrode is generally very sluggish. The measuring electrode is very easily contaminated by insidious trace quantities of tensioactive materials that render potential-determining ions incapable of participating in the formation of a double layer at the electrode-solution interface. Furthermore, the Nernst equation cannot be expected to hold true at extremely low concentrations.[5]

E_h Readings as Empiric Observations

Media that contain large quantities of oxidizing agents certainly have high oxidation potentials, and those containing large quantities of reducing agents have low potentials. Empiric correlations between the distribution of iron species and the distribution of redox potentials may sometimes be feasible. A quantitative interpretation, however, with respect to solution composition, from E_h data of natural media does not appear to be justified. In addition to their value with solutions for which the variables are known and controlled, E_h measurements may serve as valuable tools with systems that are well

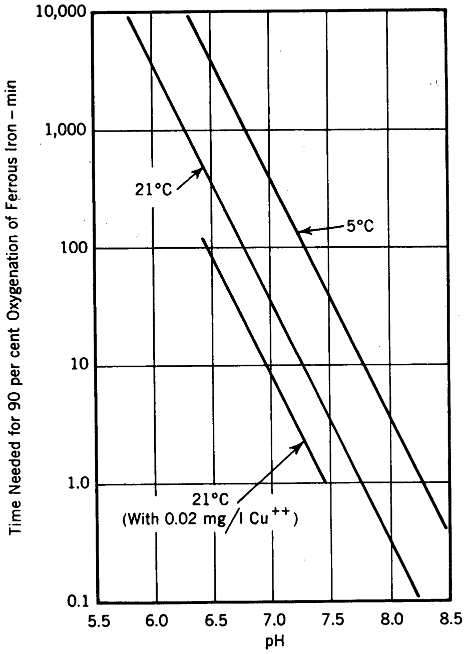

Fig. 8. Oxygenation Time as a Function of Temperature and pH

The data pertain to air-saturated HCO_3^- solutions.

poised—for example, the control of CN^- oxidation by Cl_2 or the reduction of CrO_4^{--} to $Cr(OH)_3$ in industrial wastes.

It is not the writer's intention to discourage entirely the use of redox potential measurements, but it is deemed necessary to point to some of the difficulties of measurement and interpretation. Frequently, under favorable conditions, E_h readings can supplement, but seldom entirely replace, the analytic determination of individual solution components. A trustworthy analysis of some of the pertinent constituents of the water—dissolved O_2, H^+, S^{--}, NO_2^-, NH_4^+, Fe^{++}, and Fe^{+++}, for example—is generally more informative than an E_h reading. The stability field diagram, which indicates the different equilibria that must be considered, will be a valuable tool in the interpretation of analytic findings.

The difficulties of collecting undisturbed samples for analytic purposes are appreciated. Thus, methods that involve the introduction of electrodes without contamination into the natural media are most appealing. Although the glass electrode, if used with necessary precautions, has proved to be sufficiently specific and sensitive, the platinum electrode lacks specificity. There is a pressing need to develop electrodes and monitoring systems that permit specific measurements of individual solution components *in situ*. Some progress has been made in the development of a reliable oxygen electrode,[8] and satisfactory electrodes are now available for the measurement of a few anions such as chloride and sulfide. Current research on ion-exchange membrane electrodes may lead to the development of additional specific measuring devices in the near future.

Summary

It is not intended to detract in any way from the significance of Hem's contribution on the use of stability field diagrams of iron systems. The value of potential-pH diagrams consists primarily in providing a complementary mode for the interpretation of observed facts. The measurement of E_h in natural media is plagued with many difficulties. An unambiguous interpretation of E_h readings in natural waters that contain numerous reacting redox components, which are neither known nor controlled, is not possible. There remains a well defined need for the development of specific electrodes that permit the measurement of the individual components of natural waters *in situ.*

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