Restraints on Dissolved Ferrous Iron Imposed by Bicarbonate Redox Potential, and pH

By J. D. HEM

CHEMISTRY OF IRON IN NATURAL WATER

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CONTENTS

ILLUSTRATIONS

TABLES

CHEMISTRY OF IRON IN NATURAL WATER

RESTRAINTS ON DISSOLVED FERROUS IRON IMPOSED BY BICARBONATE, REDOX POTENTIAL, AND pH

By John D. Hem

ABSTRACT

Chemical equilibrium involving carbon dioxide, bicarbonate, carbonate, and pH influences the amount of ferrous iron in much natural water. Values of pH computed from assumed equilibrium involving calcite or siderite approximate measured values of pH in 13 of 20 samples of ground water from different geologic terranes; thus, some degree of equilibrium probably existed. Two samples were supersaturated and five were undersaturated with respect to both calcite and siderite. Failure to reach equilibrium may result from absence of the minerals in the aquifer, unrepresentative analytical data, lack of reaction time, or chemical complexing.

At equilibrium, pH and iron content provide a basis for estimating the Eh (redox potential) of ground water. If much bicarbonate is present, however, the amount of iron dissolved may not change with change in Eh. For three samples from artesian wells, the Eh values measured in the field and believed to be valid ranged from +0.10 to +0.13 v (volt); they were no more than 0.03 v higher than the Eh values computed from the pH and bicarbonate and iron content. The available data are not complete enough to evaluate the differences. The measured Eh (0.28 v) of water from a pumped water-table well was 0.18 v higher than the computed value. This difference was probably due to the effect of oxygen from the atmosphere on the measurement.

PURPOSE AND SCOPE

Natural water contains dissolved ions that may affect the behavior of iron directly or indirectly. In this paper, the interrelations among pH, carbonate, bicarbonate, carbon dioxide, and ferrous iron, and the effects of the equilibria on estimates of Eh are explored by applying principles of theoretical chemistry to chemical analyses of 20 groundwater samples. These samples represent a wide variety of geologic and hydrologic conditions.

Another study (Hem and Cropper, 1959) in this series of research reports on the chemistry of iron in natural water emphasizes the effects of redox potential and pH.

CHEMICAL EQUILIBRIA IN GROUND WATER

Iron as well as other cations and anions in solution in natural ground water, must be derived from solid-phase rock minerals with which the water has been in contact. However, the chemical reactions that dissolve or deposit iron are more readily reversible than those that dissolve or deposit many other ions, and the amount of iron present is very sensitive to certain features of the water and to the rock composition at the point where the sample is obtained. These chemical reactions may closely parallel the reactions in solid-solute-solvent closed systems that chemists have reproduced and studied in laboratories for many years. Chemical thermodynamics can readily be applied to dilute solutions included in such systems.

The principal equilibria associated with solution or deposition of iron in ground water include: (a) hydrolysis and precipitation of hydroxides, (b) solution and precipitation of carbonates, (c) oxidation-reduction reactions, (d) solution and precipitation of sulfides, and (e) formation of complex ions and chelation. These equilibria are interrelated, and several may exist together in some ground water. Most chemical reactions involving iron are relatively rapid, at least when compared with the length of time most ground water has been in contact with soil and rock minerals. In general, the period from the time water enters an aquifer until it is withdrawn is fairly long unless the recharge area is very close to the point of discharge.

Huber and Garrels (1953) found that equilibrium in systems involving iron and hydrogen ions was reached rapidly in the laboratory, but equilibrium was more difficult to attain and was reached more slowly when carbon dioxide was present. They were unable, however, to attain such an equilibrium in systems involving sulfate reduction. Bacterial action is reported by Carroll (1958) to be important in sulfate reduction and, in general, to be effective in reducing iron in rock and soil.

The facts support the fundamental assumption that a chemical equilibrium exists between the dissolved iron and other solutes in ground water and the solid-phase minerals in the aquifer. This equilibrium is required before thermodynamic computations can be made.

In deriving equilibrium constants, the solid-phase material participating is assumed to be present at "unit activity." Unit activity can be assumed when an excess of the pure substance is present. Examination of the rock material in contact with the water will indicate if the assumption is reasonable. In the absence of direct information about the solid-phase mineral, an equilibrium calculation based on the chemical analysis of the water and assumed presence of the solid may still give useful information.

A water analysis does not always show the exact composition of the water in the aquifer. For studies involving iron, special attention to sampling and selection and treatment of analyses may be needed.

The standard temperature for thermodynamic computation, which is 25°C (about 77°F), is used in this study. Temperature changes or differences in the usual range of nonthermal ground water probably would not seriously affect the results. The standard pressure for these computations is 1 atmosphere, which is closely approached in unconfined water but may be exceeded in artesian systems.

SOURCES OF HYDROGEN IONS

The pH of ground water is fixed as a result of the chemical equibria that exist among solutes, solid-phase or gas-phase material in contact with the solution, and the solvent itself. The pH is the negative logarithm of the effective hydrogen-ion concentration; that is, it represents an activity or thermodynamic concentration rather than a stoichiometric concentration. Dissolved iron is generally present in relatively minor amounts; other constituents, present in larger amounts, are generally the principal factors that determine the pH of the solution. Carbon dioxide in solution as undissociated carbonic acid and as bicarbonate and carbonate ions is the buffering system that controls the pH of most natural water.

SOURCES OF CARBON DIOXIDE IN NATURAL WATER

The most obvious source of carbon dioxide in natural water is the atmosphere, whose normal carbon dioxide content is 0.03 percent, by volume. Water in contact with the air is thus under a partial carbon dioxide pressure of 3×10^{-4} atmospheres. The amount of carbon dioxide that will be in solution depends on the temperature; a greater amount goes into solution as the temperature decreases. At constant temperature, however, the amount in solution is a function of the partial pressure of carbon dioxide. By the process of photosynthesis, plants utilize carbon dioxide from the atmosphere and by the process of respiration give up some carbon dioxide to the air in pore spaces in the soil around plant roots. Decay of organic matter in the soil also produces carbon dioxide. Soil air, therefore, may be as much as 10 to 100 times richer in carbon dioxide than the atmosphere. Mohr (1938, p. 68–69) states that soil air generally contains 0.1 to 0.5 percent of carbon dioxide by volume.

Most natural water has had at least a short contact with the soil and its carbon dioxide-rich air. Water that moves directly to surface streams as runoff has less opportunity for carbon dioxide enrichment than water that seeps through the soil into ground-water reservoirs because of the difference in time of contact with the soil.

DISSOCIATION OF CARBONIC ACID

The buffer system in natural water is evaluated in an analysis by measuring the initial pH and by titrating the solution with acid to a pH of about 4.5 to convert all the bicarbonate to undissociated carbonic acid. The results are expressed in terms of bicarbonate and carbonate ions in the analyses of the Geological Survey. "Free" carbon dioxide, or undissociated carbonic acid, is difficult to determine and often is not reported, but it can be calculated from the initial pH and the bicarbonate and carbonate concentrations for most water of low or moderate concentration.

The dissociation of carbonic acid takes place in two steps:

$$H_2CO_3 \rightleftharpoons HCO_3^{-1} + H^{+1}$$

$$HCO_3^{-1} \rightleftharpoons CO_3^{-2} + H^{+1}$$

Equilibrium constants for these steps are given by Latimer (1952) as 4.16×10^{-7} and 4.84×10^{-11}, respectively. In a solution subject to a constant partial pressure of carbon dioxide and in contact with inert solids, the proportions of dissolved species—carbonic acid, bicarbonate, and carbonate—at any pH can be computed from the equations

$$\frac{[HCO_3^{-1}]\,[H^{+1}]}{[H_2CO_3]} = 4.16 \times 10^{-7}$$

and

$$\frac{[CO_3^{-2}]\,[H^{+1}]}{[HCO_3^{-1}]} = 4.84 \times 10^{-11}$$

Quantities enclosed in brackets represent activities or thermodynamic molal concentrations. The sum of the dissolved species in the solution is a function of the partial pressure of carbon dioxide. For any partial pressure and pH, therefore, the amounts of H_2CO_3, HCO_3^{-1}, and CO_3^{-2} present can be calculated.

The values resulting from this calculation are thermodynamic concentrations, which differ from the stoichiometric concentrations of bicarbonate and carbonate available from chemical analyses. The stoichiometric concentrations can be converted to thermodynamic concentrations by the use of activity coefficients. Procedures for computing activity coefficients for the ions present in natural water are described on pages 39–40.

The foregoing discussion of the dissociation of carbonic acid was simplified by assuming that all the dissolved carbon dioxide combines with water to form carbonic acid, although, actually, only about twothousandths of the carbon dioxide does. The dissociation constants were computed using the same assumption, so that the equilibrium between dissolved carbon dioxide and undissociated carbonic acid did not affect the results.

EQUILIBRIA INVOLVING SOLIDS AND SOLUTES IN NATURAL WATER

Dissociation of carbonic acid is generally the most important source of hydrogen ions in natural water. However, the amount retained in solution in effective form, as measured by the pH, is controlled by chemical reactions and equilibria involving hydrogen ions and the various rock minerals with which the solution may come in contact.

A simple expression of the type of equilibrium involved is

$$RCO_3+H^{+1}\rightleftharpoons HCO_3^{-1}+R^{+2}$$

where *R* represents alkaline earths, ferrous iron, or other divalent cations. In a system where carbon dioxide is present in excess and at a relatively high partial pressure, as in well-leached soil or subsoil zones, the equilibrium will be shifted to the left and the hydrogen-ion concentration will be high. If, however, the external supply of carbon dioxide is restricted, as it generally is below the zone of saturation in the ground-water reservoir, and if a relatively plentiful supply of solid-phase material that will react with hydrogen ions is available, the equilibrium will tend to be displaced to the right. In general, a low pH in ground water would be favored by relatively rapid circulation of water in a humid area having abundant vegetation and a geologic terrane that is impoverished in a solid-phase carbonate or other mineral readily acted upon by hydrogen ions. Converse areal conditions would tend to favor higher pH values.

Among the carbonate minerals common in many types of rocks are calcite and aragonite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$], siderite ($FeCO_3$), and magnesite ($MgCO_3$). Calcite is probably the most abundant of these minerals and is likely to be involved in the equilibria that control the pH of water in all limestone and in many sedimentary and a few igneous terranes. The equilibrium reaction between calcite and water containing hydrogen ions is represented as follows:

$$CaCO_3+H^{+1}\rightleftharpoons HCO_3^{-1}+Ca^{+2}$$

If an excess of calcite is present, an equilibrium constant, *K*, can be computed for this reaction from free-energy data and from the relationship

$$-\log K=\frac{\Delta F^\circ}{1.3643}$$

where ΔF° is the standard free-energy change for the reaction. K can also be computed from published values for the solubility product of calcite and the second dissociation constant for carbonic acid. In either computation, the value for K obtained is about 0.97×10^2.

With the equilibrium constant known, the degree to which water is in equilibrium (saturated) with calcium carbonate (as calcite) may be calculated from the analytical data for the water. A procedure suggested by Langelier (1936) has been widely used in evaluating the stability of water that has been softened in treatment plants. In the usual computation, an equilibrium pH is calculated and compared with the measured pH. If the calculated pH exceeds the measured pH, the water is capable of dissolving more calcite. If the measured pH is greater than the calculated pH, the water is supersaturated and will tend to deposit calcium carbonate. The difference between the measured and calculated pH values is commonly called the "saturation index." A high saturation index indicates a high degree of instability and the likelihood of solution or precipitation of carbonate.

For ground water in pure calcitic limestone, the relationship among the active concentrations is as follows:

$$\frac{[HCO_3^{-1}][Ca^{+2}]}{[H^{+1}]} = 0.98 \times 10^2$$

Water in contact with any rock rich in calcite should approximate the same equilibrium. Much sandstone, because of its carbonate cementation, and much shale is rich in calcite and other carbonates. Calcite is a rarer constituent of igneous rocks; but it may be present in the openings through which water moves, having been deposited from solutions that have circulated through the rocks.

Equilibrium calculations for calcium carbonate have much practical value in studies of the chemical relationships among solutes and aquifer minerals. Similar calculations can be applied to iron in systems where ferrous carbonate may occur. Siderite (ferrous carbonate) is often associated with calcite, especially in sedimentary rocks, and may be a likely solid phase in carbonate-rich rocks when the environment is relatively reducing. These conditions should be relatively common in ground-water aquifers. Siderite is attacked in the same way as calcite in the presence of hydrogen ions:

$$FeCO_3 + H^{+1} \rightleftarrows Fe^{+2} + HCO_3^{-1}$$

The equilibrium constant for this reaction, calculated from the free-energy data, is 0.46 (Latimer, 1952). This constant indicates that the equilibrium is displaced to the left to a greater degree than the equilibrium for calcite. Water in equilibrium with both calcite and siderite would contain about 200 times as much calcium as iron, as the 2 constants differ by about 2×10^2.

ACTIVITY COEFFICIENT COMPUTATIONS

Before equilibrium constants can be applied to chemical analyses of ground water, activities or thermodynamic concentrations must be calculated from the analytical, or stoichiometric, concentrations. According to the theory of Debye and Hückel, strong electrolytes in solution are fully dissociated into ions, but the movement of these ions is restricted by interionic forces whose intensity depends upon the ionic size and the charge. Generally, the intensity of the interionic forces increases as the concentration of the solution increases. The activity coefficient, which can be computed from the characteristics of the solution, is used to convert the analytical results to activities. At infinite dilution, the activity coefficient is unity, and the thermodynamic concentration is, therefore, equivalent to the stoichiometric concentration.

In most published reports in which thermodynamic computations are applied to natural water, unit-activity coefficients have been assumed, and it has been stipulated that the results are approximations and that the procedure should not be used for water having dissolved-solids concentrations of over 500 ppm (parts per million). The computation of activity coefficients is a relatively simple procedure, however, and permits theoretical computations with useful accuracy for water containing more than 500 ppm of dissolved solids.

The activity coefficient, γ, for any ion is computed from the following equation, which is based on the Debye-Hückel theory of interionic attraction:

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

where A is a constant relating to the solvent, whose value for water at 25°C is 0.5085; z is the ionic charge; μ is the ionic strength of the solution; B is a constant relating to the solvent, whose value for water at 25°C is 0.3281×10^8; and a_i represents the effective diameter of the ion in solution. Empirical values for these constants are given by Klotz (1950), who selected them from the literature. The ionic strength of a solution is computed from the expression

$$\mu = \frac{m_1z_1^2 + m_2z_2^2 + \ . \ . \ . \ m_iz_i^2}{2}$$

where m is the molality and z the ionic charge of each ion species present in solution. The subscripts refer to these species. To compute μ values from water analyses, the molarity of each ion (essentially equal to molality for present purposes) is first obtained by dividing its concentration in equivalents per million by the ionic charge multiplied by 10^3. Thus, for calcium, 2.00 epm is equivalent to a concentration of 0.001 molar. For determining activity coefficients, ionic strength values need be carried only to 2 significant figures, and generally only the 4 to 6 ions present in major proportions need to be considered.

The Debye-Hückel expression is applicable to solutions whose ionic strength is less than about 0.1. A solution of sodium and chloride ions whose ionic strength is 0.1 has a dissolved-solids concentration of 5,800 ppm. However, a solution of magnesium and sulfate ions of the same ionic strength would contain only about 3,000 ppm of dissolved solids. Natural water, in which the solutes are mixtures of various monovalent and divalent ions, generally would fall between these limits at an ionic strength of 0.1. Useful computations of activity coefficients can be made, therefore, for most potable and brackish water. For solutions with ionic strengths greater than 0.1, no satisfactory theoretical treatment has yet been developed. Therefore, more highly mineralized water is not considered in this discussion.

Figure 3 is a graph based on the Debye-Hückel expression, from which values for the activity coefficient for the ions considered in this discussion can be determined from the computed ionic strength. The divalent ferrous and calcium ions have an activity coefficient considerably less than one even at 0.01 ionic strength. Activity coefficients are even smaller for ferric iron, but this form is not an important part of the total iron activity in most natural water.

EQUILIBRIUM COMPUTATIONS APPLIED TO GROUND WATER

Analytical data for 20 ground-water samples from a variety of geologic formations in the United States are given in table 1. The samples were collected and analyzed by the Geological Survey. All contained more than 0.10 ppm of iron at time of sampling.

The pH values given in the table for analyses 4, 5, 8, 11, 17, 19, and 20 were measured in the field when the samples were collected. These values are probably representative of the water in the aquifer. The pH measured when the analysis is begun in the laboratory is nearly the same as the field value for many samples of ground water. However, for samples of weakly buffered water or of water containing large amounts of calcium and bicarbonate, the pH may change during storage, and laboratory measurements may differ considerably from field measurements.

TABLE 1.—*Determined and computed chemical data for selected iron-bearing ground water*

Analysis	Source of water	Total dissolved solids (ppm)	Ionic strength (μ)	Measured pH	Computed activity (ppm)			Computed equilibrium pH		Eh (volts)	
					HCO_3^{-1}	Fe^{+2}	Ca^{+2}	Siderite	Calcite	Estimated	Measured
1	Well, Fulton, Miss.; Tuscaloosa formation; micaceous sand, locally lignitiferous	44	0.0010	6.3	29	9.5	7.2	6.8	9.1	0.16	----------
2	Well, Middletown, Del.; greensand, overlain by Pleistocene sediments	73	.0014	5.8	19	4.8	6.0	7.2	9.3	.27	----------
3	Well, Cusetta, Ga.; Tuscaloosa formation; arkosic sand and clay lenses	148	.0018	7.1	56	3.6	21	6.9	8.3	----------	----------
4	Well, El Paso County, Colo.; Dawson arkose; detritus from igneous rock	80	.0018	6.1	45	.70	9.1	7.7	8.8	.27	----------
5	Well, Sonoma County, Calif.; volcanic rock; tuff, tuff breccia, basalt, andesite, and rhyolite	178	.0020	7.3	76	.14	6.1	8.2	8.7	.08	----------
6	Well, Hot Springs National Park, Ark.; Bigfork chert; chert interbedded with small amount shale and limestone	134	.003	6.5	65	.75	21	7.5	8.3	.19	----------
7	Cold Water Spring, Anniston, Ala.; Weisner quartzite; sandstone and local shale beds	108	.0032	7.7	119	.19	18	7.8	8.1	.02	----------
8	Indian Springs, Nye County, Nev.; rhyolite colluvium	224	.0042	7.6	123	.17	6.2	7.9	8.5	.04	----------
9	Well, Pullman, Wash.; Columbia River basalt	236	.0048	7.7	192	.38	16	7.3	7.9	----------	----------
10	Well, Vesper, Wisc.; Precambrian igneous rocks, clay, and other decomposition minerals from granite and gneiss	175	.0049	6.6	112	5.3	27	6.4	7.9	----------	----------
11	Well, Weber County, Utah; Lake Bonneville beds	337	.0068	7.7	206	.70	28	7.0	7.6	.10	0.11
12	City well, Quinlan, Okla.; Whitehorse sandstone	298	.008	8.2	255	.40	35	7.2	7.4	----------	----------
13	Well, Mackinaw City, Mich.; Mackinac limestone; brecciated limestone, dolomite, chert, shale, and gypsum	306	.009	8.0	200	.39	39	7.3	7.5	----------	----------
14	Well, Morrilton, Ark.; Quarternary alluvium	393	.010	7.1	322	6.0	69	5.9	7.0	----------	----------
15	Well, Vandalia, Ohio; Niagara limestone; limestone and interbedded shale overlain by glacial till	465	.014	7.3	467	3.3	65	6.0	6.9	----------	----------
16	Well, Graham County, Kans.; Niobrara formation; shale, limestone, and marl	685	.015	8.2	350	.57	34	6.9	7.3	----------	----------
17	Well, Park County, Mont.; Livingston formation; andesitic tuffs, agglomerates and tuffaceous sandstone and shale	800	.020	7.2	339	.11	83	7.6	6.9	.10	.28
18	Well, Bureau, Ill.; Niagara group; dolomitic limestone	2,140	.032	8.3	511	.31	6.6	7.0	7.9	----------	----------
19	Well, Weber County, Utah; Lake Bonneville beds	2,340	.039	7.7	219	.71	63	7.0	7.2	.10	.13
20	Well, Weber County, Utah; Lake Bonneville beds	2,840	.046	7.4	98	1.5	89	7.0	7.4	.09	.10

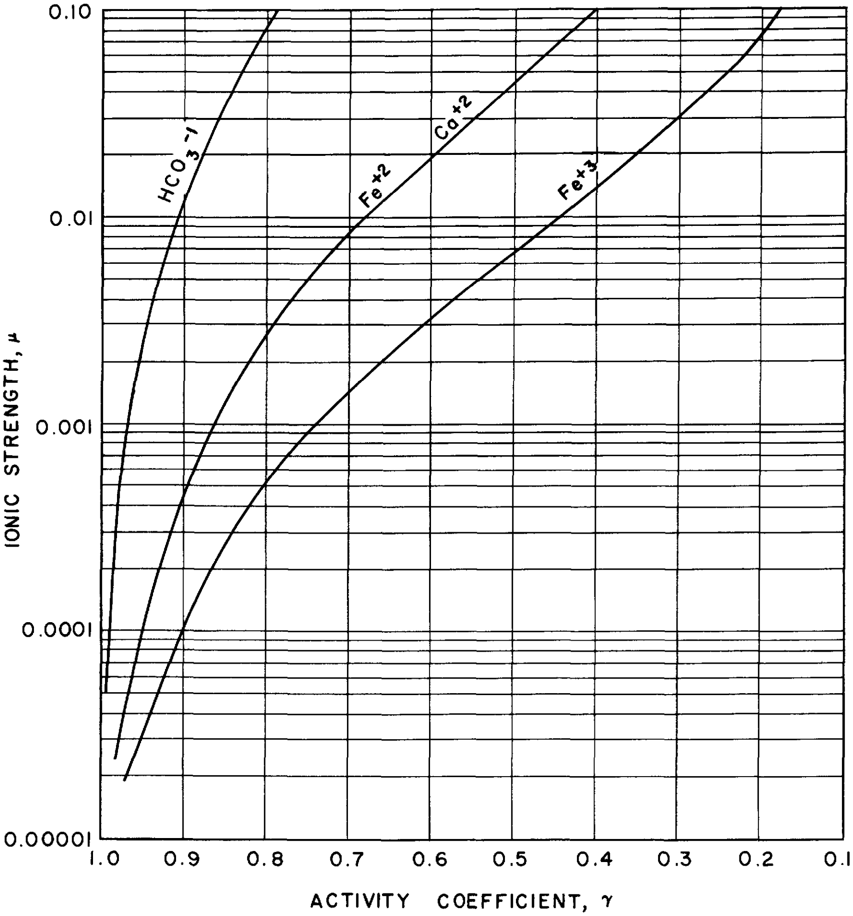

FIGURE 3.—Relation of activity coefficients for bicarbonate, calcium, and ferrous and ferric iron to ionic strength of solutions.

In all, or nearly all, the water samples, the iron had completely precipitated when the analysis was made. That the water was clear at the time of sampling, however, indicates that all the iron was in solution in the water in the aquifer. The iron activities reported in the table as Fe^{+2} were computed from calculated ionic strengths and γ values in figure 3. They represent all the iron originally present, which, as Hem and Cropper (1959) point out, must be in the ferrous form. The precipitation in sample bottles results from oxidation and hydrolysis and can be represented as

$$Fe^{+2}+3H_2O \rightleftharpoons Fe(OH)_3+3H^{+1}+e^{-1}$$

where *e* is the unit negative charge lost by each ferrous ion upon oxidation to the ferric state. Ferrous carbonate is not stable under oxidizing conditions; hence, it is not likely to be formed in water-sample bottles. The oxidation and precipitation of each ferrous ion make three hydrogen ions available. When these reactions occur in water-sample bottles, the pH may change appreciably. For example, the precipitation of 5 ppm of iron would be equivalent to converting about 18 ppm of bicarbonate ions to carbonic acid; and, if the initial bicarbonate content of the water is relatively low, the iron oxidation and precipitation could decrease the pH of the water sample drastically.

Samples represented by analyses 1 and 2 in table 1 are likely to have had a higher pH at time of sampling than at time of measurement in the laboratory. In these two analyses, the initial pH could have been half a unit or more higher than the figures given in the table, whereas the observed pH values given for the other analyses probably are more nearly representative of aquifer conditions.

Activity values for bicarbonate and calcium have been calculated for each analysis and are given in table 1.

The two computed pH values in table 1 are convenient indices of the degree to which the water may be in equilibrium with solid-phase carbonate. The computed pH values are obtained from the two equilibria for calcite and siderite, which reduce to the forms

$$pH = -\log \frac{[Fe^{+2}][HCO_3^{-1}]}{4.6 \times 10^{-1}}$$

and

$$pH = -\log \frac{[Ca^{+2}][HCO_3^{-1}]}{0.97 \times 10^{2}}$$

CAUSES OF NONEQUILIBRIUM CONDITIONS

If the 1 measured and 2 computed pH values agree to within ±0.5 pH unit, the chemical equilibria involving calcite and siderite would seem to be applicable, especially in rocks where carbonate is a major constituent. Agreement of the measured pH with 1 of the computed pH values could be indicative of the domination of the system by only 1 of the 2 carbonates.

Disagreement between measured and computed pH values can be attributed to many possible conditions. Some of the more important possibilities are the following:

1. The measured pH does not represent conditions in the aquifer. This explanation is likely if the water is supersaturated or poorly buffered (low bicarbonate) and if the measurement of pH was made in the laboratory rather than at the time of sampling.
2. Determined values of bicarbonate, iron, or calcium are not representative of conditions in the aquifer. Careful sampling and handling of samples should make this explanation unlikely.

3. Calcite or siderite are not present in the aquifer in amounts necessary to establish equilibrium or are not available for contact by the water. This explanation is the most likely for many samples of unsaturated water.
4. The iron or calcium in solution is in equilibrium with a solid phase other than siderite or calcite. Probably iron oxides and hydroxides or sulfides are dominant in some aquifers, and dolomite or other carbonates are not uncommon.
5. Travel or contact time in the aquifer was too short for equilibrium to be reached. This explanation may be applicable where the sampling point is close to the recharge point or where water moves in large channels in limestone. Generally, if these conditions occur, they will be indicated by field evidence.
6. Complex formation or chelation may influence the behavior of iron, or some iron may be present as a colloid. This is likely only in water that has considerable organic matter in solution and a decided color or turbidity or that has unusual amounts of inorganic ions, such as phosphate or fluoride, that can form complexes.
7. If the iron-bearing minerals contain impurities, the activity of iron in the solid phase may not be unity as is assumed in equilibrium calculations but may instead be proportional to the mole fraction of iron in the mineral. Iron itself could be present as an impurity in calcite, replacing some of the calcium ions in the crystal lattice. The effect of impure minerals may be important.

CALCITE-SIDERITE SATURATION-INDEX GRAPH

Results of saturation-index computions based on equilibria involving both calcite and siderite are shown in figure 4 for the 20 analyses in table 1. In the diagram, calcite saturation is indicated on the Y axis and siderite saturation on the X axis as the difference between computed and observed pH. A central band, one pH unit wide along each axis, represents essential equilibrium with respect to the calcite or siderite. The 4 quadrants of the plotting field, lettered A to D, outside the equilibrium areas represent different kinds of nonequilibrium conditions with respect to the 2 carbonates.

Quadrant A represents supersaturation with respect to both siderite and calcite. This condition probably represents water brought to equilibrium with these carbonates and subsequently transported into a different environment where a higher pH is attained by loss of carbon dioxide or other means. Supersaturation may be only an apparent condition caused by the failure of the measured pH to represent accurately the actual equilibrium pH of water in the aquifer.

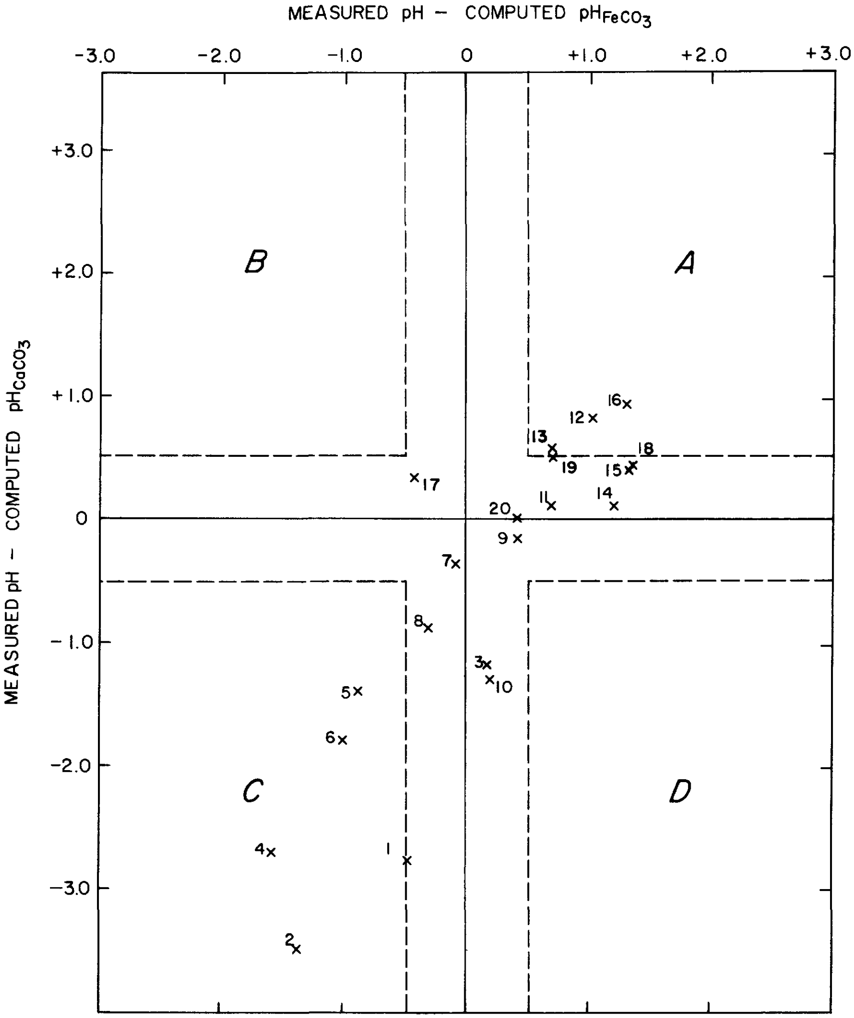

FIGURE 4.—Dual saturation-index diagram for calcite and siderite equilibria in natural water. Area, one pH unit wide, between dashed lines represents essential equilibrium; quadrants A to D represent different kinds of nonequilibrium; numbers represent samples described in table 1.

Quadrant B represents supersaturation with respect to calcite but undersaturation with respect to siderite. Analyses plotted in this area could represent water exposed to an environment rich in carbonates that contained relatively little iron. Other explanations of this condition are possible. None of the 20 analyses in table 1 plot in this area, probably because all are of iron-bearing water. Not much iron would be expected in water from environments with a low iron content.

Quadrant C represents undersaturation with respect to both siderite and calcite. An analysis plotting here probably represents water that has come from an environment where carbonates are impoverished or where calcium and iron occur in other forms. Water that has not reached equilibrium because of a short time of contact with carbonates would also probably fall in this quadrant. Water of this type could have a pH value further from equilibrium than most others; analyses in figure 4 that plot furthest from the center are in this quadrant.

Quadrant D represents supersaturation with respect to siderite and undersaturation with respect to calcite. These conditions probably are unusual because they imply a relatively high degree of enrichment of siderite with respect to calcite in the rock material. None of the analyses in table 1 plot in this area.

The analyses furthest from equilibrium plot in quadrant C and represent water from the Dawson arkose, a greensand overlain by Pleistocene sediments, the Tuscaloosa formation, the Bigfork chert, and the Sonoma volcanics. None of these rocks are expected to have a particularly high carbonate content. Conversely, water from carbonate rocks generally plots near the center of the diagram or in the area of supersaturation. The most dilute water plots in quadrant C (unsaturated with respect to both types of carbonate).

If water plots in quadrants B or C of figure 4, the computation of Eh on the basis of iron content is fairly accurate, because the assumed equilibrium will not be affected by precipitation of ferrous carbonate. Water that appears to be supersaturated (quadrants A or D) with respect to ferrous carbonate is doubtful as an indicator of Eh. Water that is near saturation, however, could give useful Eh estimates under some conditions. The diagram is useful in considering the chemical factors that produce iron-bearing water. However, the data in table 1 include so many uncertainties that few firm conclusions can be made.

In many environments, the Eh is too high (too oxidizing) to permit saturation of the water with respect to siderite. Ferrous carbonate is not likely to be precipitated where oxidation can occur. The much less soluble ferric hydroxide is the stable form in contact with air.

Although the chemical behavior of iron in ground-water systems is subject to factors other than solution and precipitation of carbonates, the mechanisms involved and the techniques of evaluating the degree to which the iron is in equilibrium with other components of the solution and of the aquifer constitute a part of the full description of the chemistry of iron in natural water.

RELATIONS AMONG REDOX POTENTIAL, pH, AND IRON CONTENT OF WATER CONTAINING BICARBONATE

The pH of a sample of ground water may not closely show the hydrogen-ion activity of the water in the aquifer; however, the effect of buffering is usually sufficient to prevent the pH from changing so much that a laboratory determination is useless. Measurement of redox potentials in ground water, however, presents a much greater problem. The concentrations of the ions in solution that produce a measured potential are generally very small. In an aquifer a large supply of solid material is available to replenish the dissolved oxidizable or reducible ions. The reserve supply of ions that could stabilize the Eh is like the supply of solutes that exerts a stabilizing effect on pH. This effect is called poising when related to Eh and buffering when related to pH.

When it reaches the atmosphere, ground water is generally only weakly poised. As soon as the water reaches the zone near and above the water table where oxygen is available, some oxygen immediately goes into solution and is indicated by the Eh of the solution. The water-oxygen couple can stabilize the Eh effectively as long as the water is in contact with air, because the large available supply of oxygen in the atmosphere exerts a poising effect.

Ground water containing a few parts per million of iron must have a rather low Eh in the aquifer, but as soon as the water has a chance to take up oxygen, the Eh rises. At saturation, such water can contain oxygen in a molarity 10 to 100 times greater than that of iron. The adjustment of the iron system to this new and stable Eh, which may be several tenths of a volt higher than the Eh in the aquifer, is slower but it ultimately results in the oxidation of nearly all the iron to the ferric state.

The interrelations among iron content, pH, and Eh have been discussed by Hem and Cropper (1959), who proposed a technique for computing Eh in aquifers. The measurement of Eh in water samples in the laboratory is not likely to give meaningful results because of the effect of oxygen. Field Eh measurements also may be affected by atmospheric oxygen. Measurements believed free from effects of oxygen were obtained recently by the Geological Survey when Eh electrodes were inserted in the discharge pipes of flowing artesian wells near the east shore of Great Salt Lake, Utah (analyses 11, 19, 20, table 1). All three measured values substantially exceed what the chemical analysis (field pH and laboratory iron determinations without regard to bicarbonate) indicates would be an equilibrium value of the water in the aquifer. Some of the factors that might affect the computed Eh values need to be reviewed because of this discrepancy.

EFFECT OF BICARBONATE ON Eh COMPUTATION

The computation of Eh values for ground water in its natural environment is affected by the bicarbonate content of the water. The effect is twofold because the bicarbonate helps fix the pH of the water and also restricts the solubility of the ferrous iron. The amount of ferric iron that can be retained in solution is a function of the third power of the hydrogen-ion content; hence, in systems where $Fe(OH)_3$ is present, a change in pH can produce a large change in the ferric-ferrous ion ratio, and a considerably different equilibrium value for Eh can result.

Figure 5 is a composite diagram showing curves representing the Eh values that a solution would have at equilibrium if the solution contained given activities of iron at pH values from 4 to 9. The diagram is similar to one given by Hem and Cropper (1959) except that it also denotes the effect of bicarbonate on the iron content of natural water.

The relations among the three variables—iron, Eh, and pH—can also be represented by "contours" of iron concentration in a plot having pH and Eh as abscissa and ordinate, respectively (Huber and Garrels, 1953). A variation of the plot (fig. 5) is used for estimating Eh values for water in aquifers where the pH and iron concentrations will be known. Iron and bicarbonate activities must be computed from the analytical data for each analysis before an Eh value can be estimated from figure 5.

Results of computations used in preparing figure 5 are summarized in table 2. The activity of ferric iron of 4 species in the presence of solid ferric hydroxide was obtained for each pH from 4 to 9 by assuming a solubility of 2×10^{-9} molar for ferric hydroxide (aqueous) and computing amounts of other species from the dissociation constants given by Hem and Cropper (1959). The concentrations of the ferrous species were computed by means of the Nernst equation

$$\mathrm{Eh} = \mathrm{E}^\circ + \frac{0.0592}{n} \log \frac{A_{\mathrm{Fe}^{+3}}}{A_{\mathrm{Fe}^{+2}}}$$

where E° is the standard potential of the couple considered, n is the number of electrons involved in the oxidation, and $A_{\mathrm{Fe}^{+3}}$ and $A_{\mathrm{Fe}^{+2}}$ are activities of oxidized and reduced forms of iron, respectively. Because values for $A_{\mathrm{Fe}^{+2}}$ are to be obtained, the equation is rearranged as follows:

$$\frac{(\mathrm{Eh} - \mathrm{E}^\circ)n}{0.0592} - \log A_{\mathrm{Fe}^{+3}} = -\log A_{\mathrm{Fe}^{+2}}$$

The value of n is unity for the couples considered. In determining $A_{\mathrm{Fe}^{+2}}$ for a given Eh and pH, the predominant ferric form was noted

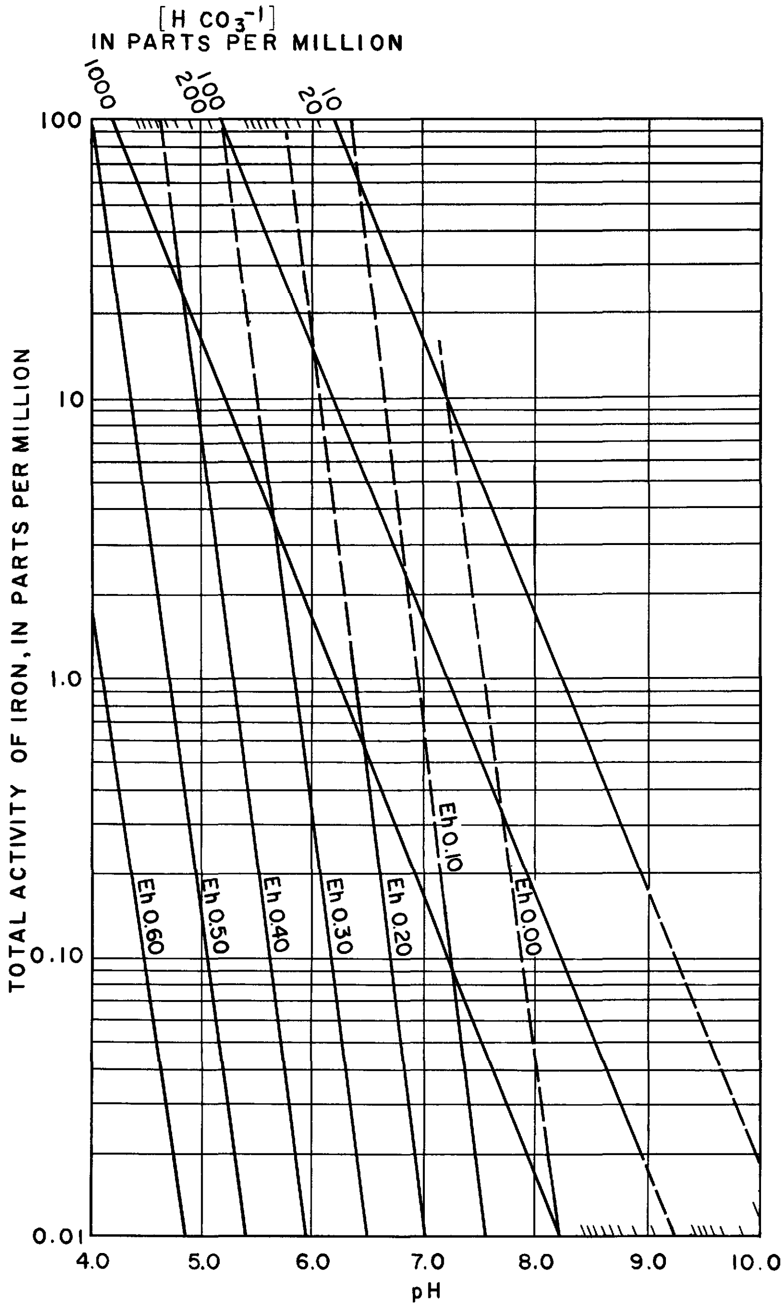

FIGURE 5.—Diagram for estimating Eh from the pH and iron content of ground water containing bicarbonate.

TABLE 2.—*Activity of iron species in solution at equilibrium as functions of Eh and pH, in absence of bicarbonate*

Eh	pH	Moles per liter								Parts per million
		Fe^{+3}	$FeOH^{+2}$	$Fe(OH^{+1})_2$	$Fe(OH)_3$ (aqueous)	Fe^{+2}	$FeOH^{+1}$	$Fe(OH)_2$ (aqueous)	ΣFe	ΣFe
+0.60	4	6.07×10^{-8}	2.25×10^{-6}	5×10^{-7}	2×10^{-9}	4.6×10^{-5}	1.0×10^{-9}	5×10^{-15}	4.9×10^{-5}	2.7
	5	6.07×10^{-11}	2.25×10^{-8}	5×10^{-8}	2×10^{-9}	5.2×10^{-8}	1.16×10^{-11}	5.8×10^{-16}	1.3×10^{-7}	.0072
	6	6.07×10^{-14}	2.25×10^{-10}	5×10^{-9}	2×10^{-9}	5.2×10^{-11}	1.16×10^{-13}	5.8×10^{-17}	7.2×10^{-9}	.0004
	7	6.07×10^{-17}	2.25×10^{-12}	5×10^{-10}	2×10^{-9}	3.7×10^{-14}	7.9×10^{-16}	4.0×10^{-18}	2.5×10^{-9}	.00014
	8	6.07×10^{-20}	2.25×10^{-14}	5×10^{-11}	2×10^{-9}	3.7×10^{-17}	7.9×10^{-18}	4.0×10^{-19}	2×10^{-9}	.00011
	9	6.07×10^{-23}	2.25×10^{-16}	5×10^{-12}	2×10^{-9}	3.7×10^{-20}	7.9×10^{-20}	4.0×10^{-20}	2×10^{-9}	.00011
+.50	4	6.07×10^{-8}	2.25×10^{-6}	5×10^{-7}	2×10^{-9}	2.25×10^{-3}	5×10^{-8}	2.5×10^{-13}	2.3×10^{-3}	128
	5	6.07×10^{-11}	2.25×10^{-8}	5×10^{-8}	2×10^{-9}	2.6×10^{-6}	5.8×10^{-10}	2.9×10^{-14}	2.6×10^{-6}	.15
	6	6.07×10^{-14}	2.25×10^{-10}	5×10^{-9}	2×10^{-9}	2.6×10^{-9}	5.8×10^{-12}	2.9×10^{-15}	9.6×10^{-9}	.00058
	7	6.07×10^{-17}	2.25×10^{-12}	5×10^{-10}	2×10^{-9}	1.8×10^{-12}	4×10^{-14}	2×10^{-16}	2.5×10^{-9}	.00014
	8	6.07×10^{-20}	2.25×10^{-14}	5×10^{-11}	2×10^{-9}	1.8×10^{-15}	4×10^{-16}	2×10^{-17}	2×10^{-9}	.00011
	9	6.07×10^{-23}	2.25×10^{-16}	5×10^{-12}	2×10^{-9}	1.8×10^{-18}	4×10^{-18}	2×10^{-18}	2×10^{-9}	.00011
+.40	4	6.07×10^{-5}	2.25×10^{-6}	5×10^{-7}	2×10^{-9}	1.1×10^{-1}	2.4×10^{-6}	1.2×10^{-11}	1.1×10^{-1}	6,150
	5	6.07×10^{-11}	2.25×10^{-8}	5×10^{-8}	2×10^{-9}	1.3×10^{-4}	2.9×10^{-8}	1.4×10^{-12}	1.3×10^{-4}	7.3
	6	6.07×10^{-14}	2.25×10^{-10}	5×10^{-9}	2×10^{-9}	1.3×10^{-7}	2.9×10^{-10}	1.4×10^{-13}	1.3×10^{-7}	.0073
	7	6.07×10^{-17}	2.25×10^{-12}	5×10^{-10}	2×10^{-9}	8.7×10^{-11}	1.9×10^{-12}	9.5×10^{-15}	2.5×10^{-9}	.00014
	8	6.07×10^{-20}	2.25×10^{-14}	5×10^{-11}	2×10^{-9}	8.7×10^{-14}	1.9×10^{-14}	9.5×10^{-16}	2×10^{-9}	.00011
	9	6.07×10^{-23}	2.25×10^{-16}	5×10^{-12}	2×10^{-9}	8.7×10^{-17}	1.9×10^{-16}	9.5×10^{-17}	2×10^{-9}	.00011
+.30	4	6.07×10^{-8}	2.25×10^{-6}	5×10^{-7}	2×10^{-9}	5.25	1.2×10^{-4}	6.0×10^{-10}	----------	----------
	5	6.07×10^{-11}	2.25×10^{-8}	5×10^{-8}	2×10^{-9}	6.2×10^{-3}	1.4×10^{-6}	7.0×10^{-11}	6.2×10^{-3}	346
	6	6.07×10^{-14}	2.25×10^{-10}	5×10^{-9}	2×10^{-9}	6.2×10^{-6}	1.4×10^{-8}	7.0×10^{-12}	6.2×10^{-6}	.346
	7	6.07×10^{-17}	2.25×10^{-12}	5×10^{-10}	2×10^{-9}	4.2×10^{-9}	9.5×10^{-11}	4.8×10^{-13}	6.7×10^{-9}	.00037
	8	6.07×10^{-20}	2.25×10^{-14}	5×10^{-11}	2×10^{-9}	4.2×10^{-12}	9.5×10^{-13}	4.8×10^{-14}	2×10^{-9}	.00011
	9	6.07×10^{-23}	2.25×10^{-16}	5×10^{-12}	2×10^{-9}	4.2×10^{-15}	9.5×10^{-15}	4.8×10^{-15}	2×10^{-9}	.00011
+.20	4	6.07×10^{-8}	2.25×10^{-6}	5×10^{-7}	2×10^{-9}	----------	----------	----------	----------	----------
	5	6.07×10^{-11}	2.25×10^{-8}	5×10^{-8}	2×10^{-9}	2.9×10^{-1}	6.5×10^{-5}	3.8×10^{-9}	2.9×10^{-1}	1,620
	6	6.07×10^{-14}	2.25×10^{-10}	5×10^{-9}	2×10^{-9}	2.9×10^{-4}	6.5×10^{-7}	3.8×10^{-10}	2.9×10^{-4}	16.2
	7	6.07×10^{-17}	2.25×10^{-12}	5×10^{-10}	2×10^{-9}	2.2×10^{-7}	4.9×10^{-9}	2.4×10^{-11}	2.3×10^{-7}	.013
	8	6.07×10^{-20}	2.25×10^{-14}	5×10^{-11}	2×10^{-9}	2.2×10^{-10}	4.9×10^{-11}	2.4×10^{-12}	2.2×10^{-9}	.00012
	9	6.07×10^{-23}	2.25×10^{-16}	5×10^{-12}	2×10^{-9}	2.1×10^{-13}	4.6×10^{-13}	2.3×10^{-13}	2×10^{-9}	.00011
+.10	4	6.07×10^{-8}	2.25×10^{-6}	5×10^{-7}	2×10^{-9}	----------	----------	----------	----------	----------
	5	6.07×10^{-11}	2.25×10^{-8}	5×10^{-8}	2×10^{-9}	1.5×10^{-1}	3.3×10^{-3}	1.6×10^{-7}	----------	----------
	6	6.07×10^{-14}	2.25×10^{-10}	5×10^{-9}	2×10^{-9}	1.5×10^{-2}	3.3×10^{-5}	1.6×10^{-8}	1.5×10^{-2}	837
	7	6.07×10^{-17}	2.25×10^{-12}	5×10^{-10}	2×10^{-9}	1.0×10^{-5}	2.2×10^{-7}	1.1×10^{-9}	1.0×10^{-5}	.56
	8	6.07×10^{-20}	2.25×10^{-14}	5×10^{-11}	2×10^{-9}	1.0×10^{-8}	2.2×10^{-9}	1.1×10^{-10}	1.4×10^{-8}	.0078
	9	6.07×10^{-23}	2.25×10^{-16}	5×10^{-12}	2×10^{-9}	1.0×10^{-11}	2.3×10^{-11}	1.2×10^{-11}	2×10^{-9}	.00011
.00	4	6.07×10^{-8}	2.25×10^{-6}	5×10^{-7}	2×10^{-9}	----------	----------	----------	----------	----------
	5	6.07×10^{-11}	2.25×10^{-8}	5×10^{-8}	2×10^{-9}	----------	----------	----------	----------	----------
	6	6.07×10^{-14}	2.25×10^{-10}	5×10^{-9}	2×10^{-9}	7.2×10^{-1}	1.6×10^{-3}	8.0×10^{-7}	7.2×10^{-1}	4,040
	7	6.07×10^{-17}	2.25×10^{-12}	5×10^{-10}	2×10^{-9}	5.1×10^{-4}	1.1×10^{-5}	5.5×10^{-8}	5.2×10^{-4}	29
	8	6.07×10^{-20}	2.25×10^{-14}	5×10^{-11}	2×10^{-9}	5.1×10^{-7}	1.1×10^{-7}	5.5×10^{-9}	6.3×10^{-7}	.035
	9	6.07×10^{-23}	2.25×10^{-16}	5×10^{-12}	2×10^{-9}	5.0×10^{-10}	1.1×10^{-9}	5.5×10^{-10}	3.1×10^{-9}	.00017

from the data in table 2 at that pH. A chemical equation showing its reduction to the corresponding ferrous form without change in pH was then written, and the value of E° determined from the relation

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

The standard free-energy change of the reaction, ΔF°, was computed from the thermodynamic data given by Hem and Cropper (1959).

Activities of ferrous species were thus computed for unit pH values from 4 to 9 at a selected Eh value. The process was repeated for Eh values 0.10 unit apart from 0 to +0.60. The sum of the seven different forms of iron for each of the pH–Eh values was then used to plot the Eh lines in figure 5.

The effect of carbon dioxide, carbonate, and bicarbonate must be considered, because besides controlling the pH, they also limit the solubility of ferrous iron. For any given pH below 9.0 and activity of bicarbonate ions in solution, the maximum activity of iron can be calculated from the equilibrium for the solution of siderite used in preparing table 1. In effect, this is a boundary that limits the direct application of the pH and iron contents alone to estimate Eh. Beyond the boundary, the activity of iron in solution is affected by the presence of solid-phase siderite as a factor in the equilibrium. The solubility of iron in this siderite region is a function of pH and bicarbonate activity, rather than of Eh.

In using figure 5 to estimate Eh values for iron-bearing water, the ionic strength of the solution should first be calculated. The activities of iron and bicarbonate present can then be determined from figure 3. The position of the bicarbonate boundary in figure 5 can be established by laying a straightedge parallel to the bicarbonate lines, in a position corresponding to the bicarbonate activity of the sample. If the iron and pH values intersect at a point to the left of the bicarbonate boundary, the Eh of the water in its environment can be estimated by its position with respect to the Eh lines.

Water samples whose iron and pH values plot to the right of the bicarbonate boundary represent conditions under which Eh computations cannot generally be made. Several possible explanations can be given for a water sample plotting in this position, which is equivalent to a water sample plotting in quadrants A or D of figure 4. Some of these possibilities are the following: (a) The iron supersaturation may result from a slow precipitation of ferrous carbonate that has not reached equilibrium, (b) the measured pH value may be higher than the actual value in the aquifer, or (c) the iron concentration may represent, in part, colloidal or complexed iron unavailable for reaction to precipitate ferrous carbonate.

The Eh values for 11 of the 20 water samples whose analyses are given in table 1 have been computed from data in figure 5, and the results are given in table 1. Also, Eh values measured in the field for four of the samples are given in table 1. For 12 of the 20 analyses, the activity of iron seems to indicate substantial supersaturation with respect to ferrous carbonate. For three water samples having a measured Eh and showing only slightly more than equilibrium amounts of iron, the Eh was read from the graph at the intersection of iron activity and calculated saturation pH for siderite. This gave a value for comparison with measured Eh, but the significance of the comparison is open to question.

The 3 possibilities listed above should be considered in connection with these 3 analyses. If actual nonequilibrium conditions exist, no estimate of Eh is possible. If the apparent supersaturation is really a result of too high a measured pH, however, an Eh could be estimated from the computed equilibrium pH for the siderite equilibrium given in table 1. If the third possibility, complexing of part of the iron, is the explanation, the activity of iron related to pH and Eh would depend on the behavior of the complex and would, therefore, seem indeterminate.

Adjustments in the pH used for the Eh calculation have a greater effect on computed Eh than adjustments to the iron activity, because of the steep negative slope of the Eh lines in figure 5.

Logarithms of the ferric-ferrous ratio are used in the Nernst equation (p. 48) to compute Eh. A difference of about 0.06 v in Eh is produced by a change in the ratio of one power of 10. Agreement between measured and computed Eh values is possible within ±0.06 v if both values are reasonably correct. Of the four measured Eh values in table 1, one value differs from the estimated value by a relatively substantial margin, but the other values agree within 0.06 v. In all four analyses, the computed Eh is lower than the measured Eh. The same tendency for measured Eh to exceed the computed value has been observed where a comparison can be made in other work done to date.

The difficulties in measuring Eh in ground-water samples in the field are substantial. The values given in table 1 represent measurements at the land surface with a battery-operated pH meter having calomel and platinum electrodes. Analysis 17 was made on water from a water-table well 80 feet deep, pumped at the rate of 50 gpm (gallons per minute). Water from this well may have been aerated, and, if so, the difference between measured and computed Eh can be easily ascribed to oxygenation of the water before and during the field measurement.

Analyses 11, 19, and 20 were made on water from flowing artesian wells, several hundred feet deep. Number 19 is of water from a well with a very small volume of flow, and number 20, a flow of only 10 gpm. Measured values of Eh are within 0.03 of agreement with calculated values. Analysis 20 plots near the center of figure 4 and seems to indicate near equilibrium with respect to carbonates, although the measured Eh exceeds the computed Eh by 0.01. Analyses 11 and 19 were made on water from the same geologic terrane as analysis 20, but they plot farther beyond the edge of the siderite equilibrium zone of figure 4. If equilibrium is assumed and an Eh is computed for the equilibrium pH given in table 2, a value of 0.10 is obtained for each water sample. The measured values are 0.11 and 0.13. Because of the uncertainties in this estimate, work done to date gives no valid comparison of measured and calculated Eh values.

SOLUBILITY OF FERRIC HYDROXIDE

The apparently consistent tendency for Eh values measured in the laboratory to exceed computed values (Hem and Cropper, 1959) suggests that some constant factor may be involved.

Several possibilities could explain this tendency. One possibility is that the low solubility of ferric oxide and hydroxide causes some uncertainty in the measurement of solubility-product values. The values in the literature range from about 3×10^{-36} (Evans and Prior, 1949) for freshly precipitated hydroxide to about 6×10^{-40} (Cooper, 1937) for aged material. For the oxide hematite, which is the dehydrated form, values are as low as 10^{-42} (Pourbaix, 1949). The form of the hydroxide most likely to occur in a ground-water environment is uncertain, but it probably would not be dehydrated.

At the beginning of this research, the value of 6×10^{-38} as given by Latimer (1952) was selected because it represented a compromise among the available values. If a solubility product an order of magnitude or so larger had been used, the agreement between computed and measured Eh would be better for most of the available laboratory results. The results of this study could be interpreted as meaning that ferric hydroxide or oxide in the solid phase of ground-water systems behaves as if its solubility product were about 10^{-36}; however, the evidence is not conclusive, because other variables may be important. Among the other possibilities are complexing reactions involving iron and the effects of impurities in the iron-bearing minerals of the aquifers studied.

IMPROVEMENT OF Eh MEASUREMENTS

More study of Eh measuring techniques as applied to ground water is needed. Evidently, the results obtained at the land surface, where the water is in contact with air, have no close relation to the values existing in aquifers. Possibly, better results could be attained by using a suitable probe in uncased wells in which the water stands at a considerable depth above the bottom of the hole.

Baas-Becking, Wood, and Kaplan (1957) report pH and Eh values for water and mud samples from various sources in Australia and New Zealand. They observed Eh values that were actually negative in some water from geothermal sources and water associated with evaporites. Methods of measurement are not given. The authors ascribe much importance to biologic factors in establishing Eh and pH, but they point out that iron systems are intimately involved.

CONCLUSIONS

The chemical relations in most natural water are relatively complex. Iron is generally present in water as an accessory or as a relatively minor constituent. The amounts present and the oxidation states are, consequently, often results of chemical equilibria that involve other ions. Because the oxidation and reduction of iron and the precipitation of ferric hydroxide are relatively rapid at pH levels common in such systems, the iron contained in natural water should generally be in chemical equilibrium with other constituents of the water and with the solid-phase material in contact with the water.

Carbon dioxide-bicarbonate-carbonate equilibria are expected in most natural water. They determine limits for solubility of iron under reducing conditions, because of their effect on pH and because of the low solubility of ferrous carbonate.

Larger amounts of ferrous iron can be dissolved in ground water as the Eh of the environment decreases. The presence of bicarbonate in an appreciable quantity, however, may prevent changes in Eh from affecting the iron content.

The techniques suggested in this report for study of ground-water systems are means for describing the chemical behavior of iron in ground water. Similar approaches may be useful in evaluating the complex chemical equilibria that control the content of other ions in solution. Conclusions that can be reached are most definite and useful if the analyses and related data show that equilibrium is closely approached. Where nonequilibrium is indicated, several possible explanations generally can be postulated.

Much of the discussion of these systems involving iron in ground water has only a theoretical basis at the present time. Chemical analyses substantiate the general applicability of the theoretical approach. However, most of the data available are not complete enough to permit a close quantitative check with theoretically derived values. More attention to the collection of chemical-quality data that reliably represent actual conditions in water in aquifers is needed before such checks can be made.

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