Chemical Properties of Ground Water and Their Corrosion and Encrustation Effects on Wells

GEOLOGICAL SURVEY PROFESSIONAL PAPER 498-D

Prepared in cooperation with the
Governments of Nigeria, the United
Arab Republic, and West Pakistan,
under the auspices of the United
States Agency for International
Development

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

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By IVAN BARNES *and* FRANK E. CLARKE

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Studies of well waters from Nigeria,
Egypt, and Pakistan and use of equilibrium
data on calcite and ferric hydroxide in
predicting magnitude of corrosion and
encrustation problems

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SYMBOLS

A^*	A constant=1824347.0.
a_o	Distance of nearest approach of dissolved species.
a,b,c	Components.
AP	Activity product.
(aq)	Dissolved aqueous species.
atm	Atmosphere, pressure unit.
B^*	A constant=50.297670.
C_p	Is the heat capacity at constant pressure.
calc	Subscript for calculated property.
CR	Ratio of cation concentration or activity actually found to cation concentration or activity at equilibrium.
D	Dielectric constant of pure water.
d	Exact differential.
d_w	Density of water.
E	Electrical potential.
E°	Standard state electrical potential.
e	Electronic charge.
e^-	Electrons involved in chemical reactions.
Eh	Oxidation-reduction potential.
Ehm	Measured oxidation potential.
EhTC	Equilibrium oxidation potential calculated for the temperature measured in the field.
Emf	Electromotive force.
eq	Subscript for equilibrium properties.
$\mathfrak{F}$	Voltgram equivalent.
G	Gibbs free energy.
G°	Standard state Gibbs free energy.
G'	Gibbs free energy at equilibrium.
GFW	Gram formula weight.
H	Enthalpy.
i,j	Species.
I, J, K	Phases.
IPY	Corrosion rate, expressed as inch penetration per year.
K	Equilibrium constant.
k	Is Boltzmann's constant.
L	A time and cross-sectional area conversion factor.
ln	Logarithm base *e*.
M_i	Amount of species *i* present.
m_i	Molality of species *i*.
mm	Millimeter.
N	Avogadro's number.
n	Number of electrons.
obs	Subscript for observed property.
P	Pressure.
pH	Negative logarithm, base 10, of the hydrogen ion activity.
ppm	Parts per million.
Q	Heat added to the system.
R	Gas constant.
r	Electrical resistance.
S	Entropy.
S°	Standard state entropy.
SCE	Saturated calomel electrode.
T	Temperature, degrees Kelvin.
T_e	Duration of exposure of corrosion test specimen.
TOT	Subscript to denote total amounts.
U	Internal energy.
V	Volume.
V°	Standard state volume.
W	Work done by the system.
W_{el}	Electrical work.
W_{exp}	Work of expansion against a pressure.
z_i	Charge on ion *i*.
α_i	Activity (molal) of species *i*.
Γ	Ionic strength.
γ_i	Activity coefficient of species *i*.
Δ	Finite change or increment.
2Θ	Twice the glancing angle in X-ray diffraction.
μ^*	Chemical potential in a half cell.
μ_i	Chemical potential of species *i*.
μ_i°	Standard state chemical potential of species *i*.
μ'	Chemical potential at equilibrium.
$\Delta\mu_R$	Sum of chemical potentials for a reaction.
$\sum\limits^{i}$	Summation over all species of type *i*.
∂	Partial differential.

HYDROLOGY OF AQUIFER SYSTEMS

CHEMICAL PROPERTIES OF GROUND WATER AND THEIR CORROSION AND ENCRUSTATION EFFECTS ON WELLS

By IVAN BARNES and FRANK E. CLARKE

ABSTRACT

Well waters in Egypt, Nigeria, and West Pakistan were studied for their chemical properties and corrosive or encrusting behavior. From the chemical composition of the waters, reaction states with reference to equilibrium were tested for 29 possible coexisting oxides, carbonates, sulfides, and elements. Of the 29 solids considered, only calcite, $CaCO_3$, and ferric hydroxide, $Fe(OH)_3$, showed any correlation with the corrosiveness of the waters to mild steel (iron metal). All 39 of the waters tested were out of equilibrium with iron metal, but those waters in equilibrium or supersaturated with both calcite and ferric hydroxide were the least corrosive. Supersaturation with other solid phases apparently was unrelated to corrosion.

A number of solids may form surface deposits in wells and lead to decreased yields by fouling well intakes (screens and gravel packs) or increasing friction losses in casings. Calcite, $CaCO_3$; ferric hydroxide, $Fe(OH)_3$; magnetite, Fe_3O_4; siderite, $FeCO_3$; hausmannite, Mn_3O_4 (tetragonal); manganese spinel, Mn_3O_4 (isometric); three iron sulfides—mackinawite, FeS (tetragonal); greigite, Fe_3S_4 (isometric); and smythite, Fe_3S_4 (rhombohedral)—copper hydroxide, $Cu(OH)_2$; and manganese hydroxide, $Mn(OH)_2$, were all at least tentatively identified in the deposits sampled.

Of geochemical interest is the demonstration that simple stable equilibrium models fail in nearly every case to predict compositions of water yielded by the wells studied. Only one stable phase (calcite) was found to exhibit behavior approximately predictable from stable equilibrium considerations. No other stable phase was found to behave as would be predicted from equilibrium considerations. All the solids found to precipitate (except calcite) are metastable in that they are not the least soluble phases possible in the systems studied.

In terms of metastable equilibrium, siderite and ferric hydroxide behave approximately as would be predicted from equilibrium considerations, but both are metastable and the presence of neither would be anticipated if only the most stable phases were considered. The behaviors of none of the other solids would be predictable from either stable or metastable equilibrium considerations.

An unanswered problem raised by the study reported here is how, or by what paths, truly stable phases form if first precipitates are generally metastable.

The utility of the findings in well design and operation is in no way impaired by the general lack of equilibrium. Conditions leading to either corrosion (which is related to lack of supersaturation with protective phases), or encrustation (supersaturation with phases that were found to precipitate), or both, apparently can be identified. The application of the methods described can be of great importance in developing unexploited ground-water resources in that certain practical problems can be identified before extensive well construction and unnecessary well failure.

ACKNOWLEDGMENTS

The water well studies which yielded the data covered by this report were made in cooperation with the Governments of Nigeria, the United Arab Republic, and West Pakistan, under the auspices of the United States Agency for International Development (USAID).

The background references contain the names of many individuals who provided invaluable help from the Geological Survey of Nigeria (GSN); the Egyptain General Desert Development Organization (EGDDO); the Water and Soil Investigation Division (WASID) of the Water and Power Development Authority (WAPDA) of West Pakistan; and personnel of the respective USAID missions. These references also acknowledge help of the following U.S. Geological Survey personnel. Valuable analytical assistance was provided by Pauline Dunton, Norman Beamer and associates, Blair Jones, and Roger Wolff. Acknowledgment is made herewith to Mary E. Mrose for special instrumental analyses, to Alfred H. Truesdell and John D. Hem for their thorough reviews and technical suggestions, to Mary E. Grisak for her patient typing of clear text from manuscript, and to Norma C. Grube for her excellent technical editing, constructive criticism of composition and format, and painstaking preparation of the final manuscript.

PURPOSE AND SCOPE

The purpose of this report is to describe the chemical properties found in water yielded from wells and to relate the chemical properties of the water to corrosion and encrustation of the well components. In addition to the practical results of the study, the data also provide insight into the behavior of naturally occurring solid phases (minerals) which are of interest in geochemical considerations.

A large amount of information is needed to achieve the purpose of such a study. Detailed analytical data on the water compositions, electrochemical measurements in the field (*Eh* and pH), and field measurements of unstable constituents (HCO_3^-, dissolved oxygen, ferrous iron) all are needed properly to define the properties of the waters yielded by the wells. Chemical and mineralogic studies of the solids depositing on well parts and studies of the extent of corrosion attack and rate of corrosion attack are needed to relate chemical properties to practical consequences of corrosion or encrustation. The results reported here include all the considerations listed above, where possible, and hence provide a unique opportunity to accomplish the purpose of the report. The wells in these widely scattered localities were studied because serious corrosion and encrustation proved to be unexpected problems, and the magnitude of long-range ground-water developments warranted detailed studies at these sites. These studies are covered by Clarke (1963) and Clarke and Barnes (1964, 1965) in open-file publications of the U.S. Geological Survey.

The waters described in this report are not unstable in the sense that rapid spontaneous reactions occur. A thermodynamic treatment of the analytical data may help to explain the sluggishness of some of the reactions and the apparent failure of others to take place at all. The thermodynamic properties of the actual states may be calculated and compared to the state of equilibrium with possible coexisting solids. The calculations yield potentials existing in the solutions to drive reactions. If the potentials for a reaction are always low and the postulated reactants are present, the small values of the potentials may be regarded as presumptive evidence for a relatively fast reaction. If large potentials are found for a reaction and the postulated reactants are present, then presumably the reaction proceeds only slowly or there is unlimited supply of reactants. Direct observation is helpful in proving that the reaction does indeed occur. Hopefully, the accumulation of a large body of the kind of information that is presented here will lead to improved knowledge of how phases actually behave in the natural environment and to better understanding of geologic processes.

PREVIOUS STUDIES

Methods for the investigation of naturally occurring water have been developed for field use (Back and Barnes, 1961; Barnes, 1964). These methods are used for the measurement of the oxidation-reduction potential (*Eh*) and pH and bicarbonate (HCO_3^-) ion concentration to supplement the usual methods of chemical analysis as described by Rainwater and Thatcher (1960). By means of the more recent developments the interpretation of natural water compositions has been extended beyond the earlier excellent treatment of Hem (1959). *Eh* and pH measurement methods for natural materials also have been advanced by recent Russian work (Germanov and others, 1959; Solomin, 1965) but have served largely to classify waters or rocks as relatively reducing or oxidizing. The compilation of Baas Becking, Kaplan, and Moore (1960) listed pH and *Eh* data from natural environments; again, the variables were largely descriptive, and quantitative interpretations could not be made.

In spite of the complex systems found in nature, attempts have been made to interpret the chemical data including pH and *Eh*. To a large extent, the study here reported is an outgrowth of the pioneering work of Garrels (1960) and the numerous papers by Hem (1960 a, b, c; 1961 a, b; 1963 a, b, c, d, e; and 1964) who independently applied the same arguments to the equilibrium description of systems such as those reported here. At least partial success in interpreting the compositions of ground water was obtained by Back and Barnes (1965), Barnes and Back (1964a), Barnes and Clarke (1964), and Barnes, Stuart, and Fisher (1964). Back and Barnes in their work in southern Maryland chose an area in which limonite, lignite, and silicates predominated and the data collected and analysis, although admittedly simplified, were aimed at a resolution of the chemical behavior of limonite in natural environments. Taking the *Eh*, pH, and iron concentrations in the water and considering the ionic strength and ion pair formation, they concluded that the solubility of limonite apparently ranged between the solubility of $Fe(OH)_3$ (Hem and Cropper, 1959) and the solubility of Fe_2O_3 (hematite) given by Latimer (1952). Back and Barnes also found that, generally, the longer the contact time between the water and the lignite, the lower the *Eh* and the closer the solubility of limonite approached the limit imposed by hematite.

Barnes, Stuart, and Fisher (1964) extended the data analysis to include limonite and pyrite. They were able to show that in some cases pyrite dissolved and apparently saturated coexisting aqueous solutions by the reaction:

$$FeS_2 + 8H_2O = Fe^{+2} + 2SO_4^{-2} + 16H^+ + 14e^-. \qquad (1)$$

In separately reported work, Barnes (1965) showed that in the rapidly varying ambient of a stream under subaerial conditions calcite supersaturation could be as much as 20 times the calcium activity for the carbonate activity of the water. Back (1963) found that in the slowly varying ambient conditions of ground-water flow, the departure on the supersaturated side of equilibrium rarely exceeded twice the calcium ion activity for the carbonate ion activity found.

The papers cited and briefly summarized above differ from the usual natural water chemical studies in that they consider the behavior of phases that might occur, or are known to occur, given the composition of the water and the approximate mineralogy of the rocks. The studies also depart from the usual geologic investigation because the studies included the measurement of the chemical properties of the water coexisting with the other geologic materials found. Many precautions have been necessary in the measurements of the chemical properties of natural aqueous solutions. Barnes (1964) showed that the pH must be measured in the field. Back, and Barnes (1961) showed that the measurement of the *Eh* is, at best, time consuming. Roberson, Feth, Seaber, and Anderson (1963) showed that significant changes in HCO_3^- concentrations may occur on sample storage. Barnes and Back (1964b) have shown that ground waters in limestones may often be supersaturated with calcite, and hence aliquots for subsequent laboratory analysis for calcium should be acidified (see also Barnes, 1965). Dissolved oxygen is a notorously unreliable analysis unless done in the field with due precaution. Iron in solution in ground water is chiefly as Fe^{+2} (Barnes and Back, 1964a), and aliquots should be collected, filtered if possible, and acidified for subsequent analysis. If the pH in the field be greater than 4.0, the total iron dissolved in the original sample should be nearly all Fe^{+2} (Barnes and Clarke, 1964).

INTERCEPTION OF GROUND WATER BY WELLS

In detail, the hydrology of a single well may be quite complicated. Permeability is not uniform in all directions and at all locations within an aquifer. Not only is an aquifer generally not isotropic (nonuniform permeability), but an aquifer is usually not homogeneous, physically or chemically. As a consequence, stratification or other variation in water compositions may be expected in a single aquifer. Depending upon the distribution of permeability and its directional variation and upon the interval(s) screened in the well and the method of well operation, water of different compositions may be mixed in the well and may yield precipitates. Intermittent operation of a well further complicates the hydrology, as the well may serve as a hydraulic path for relatively rapid flow between parts of the aquifer (a flow that might occur at a very slow rate, if at all, under natural conditions). During periods of well operation the hydrology may be quite different from that during nonoperating periods.

As a consequence of the complex hydrology, the detailed chemical properties of water yielded by a well may be expected to vary with time and often to represent unnatural mixtures. It should be remembered that, however variable the hydrology and chemistry may be, the water yielded by the well may represent the solution that gave rise to troublesome corrosion or encrustation, and the water is thus of great practical importance. Geochemically, the water mixtures may represent extreme cases. If it can be demonstrated by the study of the waters yielded by the well that some reactions do not occur in spite of large potentials to drive the reactions or that other reactions are so rapid that large potentials cannot be achieved even by rapid mixing of incompatible solutions, then the results will be of geochemical importance.

METHODS OF SAMPLING AND ANALYSIS

The field methods used are those in references cited above. *Eh* was determined by the methods and with the equipment described by Back and Barnes (1961); pH and HCO_3^-, from the methods described by Barnes (1964). HCO_3^- concentrations, obtained graphically (Barnes, 1964), agreed within 1 ppm (part per million) of the results of the computer program written by Fred Sower, of the U.S. Geological Survey, for the data reported by Barnes (1965). In none of the wells was dissolved oxygen found below 10 feet from the surface when an oxygen probe with silver and gold electrode (Yellow Springs Instrument Co., Yellow Springs, Ohio) was used. Many of the chemical analyses were done in the U.S. Geological Survey laboratories, where the methods of Rainwater and Thatcher (1960) were used, and generally the results were in close agreement with analyses done in foreign laboratories by unspecified methods. Careful chemical analyses know no political boundaries.

Whether performed in the field or in the laboratory, the analysis of a water sample must be interpreted in the light of the representativeness and reliability of the sample. In general, the data obtained for this report were from samples of water discharged by flowing or pumping wells.

CORROSION TESTING

The inherent corrosiveness of water can best be studied with an electrically insulated specimen filament which eliminates the effects of long-line current, differential concentration cells, galvanic couples, and unusual velocity effects. The corrosion elements used in this study (fig. 1) consisted of 0.04-inch (1-mm)

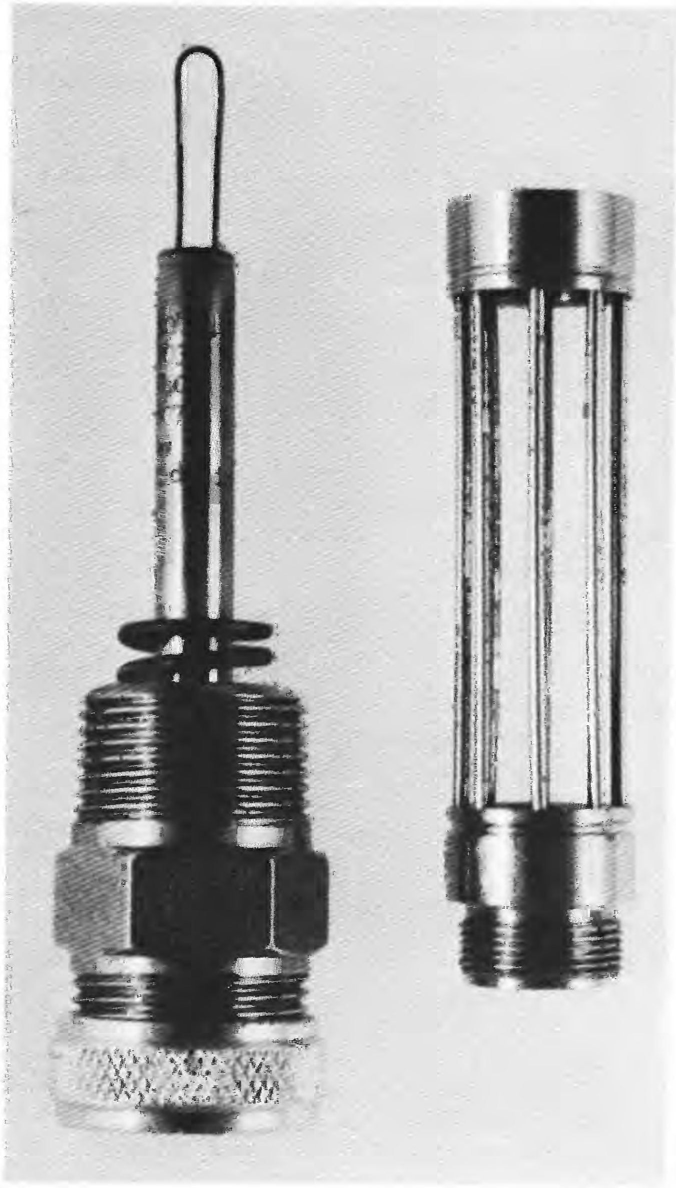

FIGURE 1.—Corrosion probe.

diameter loops of test wire inserted through the well casing or water-discharge pipe by means of a threaded probe body. One part of the loop is enclosed in a sealed tube and thus is separated from the water so that resistance changes due to temperature changes may be measured. Electrical connections between the covered and uncovered parts of the loop allow the two parts to be separate legs of a bridge circuit. Changes in electrical resistance resulting from corrosion of the test loop can be determined and converted to inch penetration per year (IPY) by the equation:

$$\text{IPY}=\frac{\Delta r}{\Delta T_e}\times L \qquad (2)$$

where:

Δr and ΔT_e = change in resistance and elapsed time of exposure, respectively;

L = a time and cross-sectional area conversion factor.

The IPY ranges of 0 to 0.002, 0.002 to 0.02, 0.02 to 0.05, and greater than 0.05 are considered to represent insignificant, moderate, severe, and extreme damage to mild steel.

The corrosion probe filament is more useful in assessing general corrosion than in predicting the extent of localized pitting. Although it cannot be used accurately to determine actual lives of well parts, it is useful in comparing several metals in a particular environment or effects of several environments on a single metal.

Metal loss data determined with corrosion probes can be related to actual metal lives of well parts only if there is some actual well field experience with the same metals, to establish relationships between corrosion of the insulated probes and the actual well construction materials. The latter, or course, are subject to other factors, such as galvanic effects, long-line currents, and concentration cells, as well as to the basic water-quality factors. Because corrosion probes generally are placed in the upper casing or discharge lines of wells, and thus sample the mixed discharge, field tests with actual well parts help one avoid overlooking severe local effects which may not be apparent in a small specimen exposed to an integrated discharge sample. Fortunately, experience in most deep-well studies has shown that waters flowing from the wells are approximately constant in chemical properties and that corrosion-probe data correlate rather well with performance of metal parts. This would appear to support the basic hypothesis of this paper: that the basic chemistry of the water discharged is as important as local effects in causing corrosion and encrustation in deep water wells and that installation of corrosion probes in discharge lines is a reasonably representative device for assessing damage in such environments.

EXAMINATION OF DEPOSITS

Solid samples of deposits from well parts were examined with a binocular microscope, and, unless otherwise indicated, small parts of each specimen were ground to silt-clay size using agate mortar and pestle or a tungsten carbide grinding vial. For examination, the ground parts of some samples were mounted on glass slides. Other powdered samples were pressed into special aluminum holders. Samples thus prepared were examined by X-ray diffraction on a Norelco recording diffractometer employing nickel-filtered copper radiation and a proportional counter for pulse-height discrimination, at scanning speeds of 1° 2Θ per minute.

Interpretations are based on comparisons with standard materials and the file-card data of the American Society for Testing and Materials (ASTM) and were checked against additional citations from the literature.

Pulse-height analysis did not entirely eliminate interference from iron fluorescence. It is unlikely that material was detected in quantities less than about 5 percent by volume. Poorly crystallized iron minerals, such as goethite (FeOOH), sometimes cannot be positively identified in amounts less than 20 percent.

Where better-resolved X-ray diffraction measurements were needed, powder samples were photographed in manganese-filtered iron radiation by Mary E. Mrose, U.S. Geological Survey. These films were then measured by Blair F. Jones and compared with film, as well as diffractometer standards. X-ray fluorescence analysis for sulfur was done by Pauline J. Dunton.

THEORY

Observations have been made of the physical and chemical properties of various aqueous solutions. A rational basis is needed for the comparison of observations to determine if any consistent relationships hold. Thermodynamic arguments seem the most reasonable bases for comparing the properties of the well waters studied because the arguments are rigorous. A direct test is also afforded of the departures from chemical equilibrium in the waters sampled. The use of thermodynamics then provides a quantitative comparison of the waters studied and also a direct test of the validity of postulated chemical equilibria.

Unfortunately, a fairly extensive derivation of thermodynamic relations is necessary. The systems studied are real and are to be compared to equilibrium states as references. There is in the literature no development of the theory needed to treat the systems here described, and thus the derivations are given.

The studies of the behaviors of naturally occurring substances have included two kinds of mineral-water reactions. The simpler type of reaction involves no electron transfer and the behavior of the solid substance can be described in terms of chemical parameters, temperature, and pressure. Calcite is an example of the simple case. Whether the reaction is written

$$CaCO_3 = Ca^{+2} + CO_3^{-2}, \tag{3}$$

$$CaCO_3 + H^+ = Ca^{+2} + HCO_3^-, \tag{4}$$

$$CaCO_3 + H_2O = Ca^{+2} + HCO_3^- + OH^-, \tag{5}$$

or other ways, tests for the behavior of calcite require knowing only the temperature, pressure, and chemical composition of the solution. The law of mass action is the basis for testing the behavior of phases undergoing simple reactions.

Equally important are reactions involving electron transfer such as, for hematite,

$$3H_2O + 2Fe^{+2} = Fe_2O_3 + 6H^+ + 2e^-. \tag{6}$$

Studies of reactions involving electron transfer require more information than the chemical composition of the solution, the temperature, and the pressure. the electrons produced are charges and induce electrical potentials so that the study of electron transfer reactions must also include a study of electrochemical properties.

Because this report is on both mass action reactions and electron transfer reactions, a general development of the theory is needed. Both types of reactions must be placed on the same formal basis to show the similarities and differences among the reactions described.

A system, as the term is used in this report, is any part of the universe isolated for consideration. The volume arbitrarily isolated may be considered theoretically or it may be isolated for measurements—physical, chemical, or both. The boundaries of the system may be fixed, as the wall of a sample bottle, or moving, as for water flowing through a chamber in which measurements are made. If the boundaries to the system are moving, care must be taken that each volume of the water occupying the chamber is the same as every other volume; thus, monitoring the water properties in time may be necessary.

If the properties of a system are constant over a period of measurement, then the system will be termed stable. From this definition of stability, various degrees of stability may be found by observations made over varying lengths of time. In the flowing system (moving boundaries) monitoring or continually measuring the properties of interest is required to determine stability.

Fixed system boundaries are no guarantee of stability of a system. For example, a water sample in a bottle may change because of intrinsic long-term instability of the sample. On the other hand, the original water may be intrinsically stable, but if it is placed in a sample bottle which contains air, the air may not be compatible (stable) with the water, and both may change in properties (react). The air-water sample interaction is an example of an unstable system containing two substances, a gas and a liquid. A clear distinction should be made between the stability of naturally occurring water in its natural environment and the stability or instability of water samples stored for subsequent analysis. If measurements of the properties of the water at the sampling site yield inconstant results during a period of measurement, then it should be concluded that the water is unstable, and great care must be exercised in the interpretation of the properties of the water. On the other hand, if a sample of water is collected and placed in a container for subsequent study, the system represented by the sample may be unstable over the period of transport to the laboratory and storage within the laboratory. In the discussion of previous studies examples are given of unstable samples. The demonstration of the stability of the sample requires proof that the measurement of properties, immediately upon capture of the sample, yield the same results as the same measurement at a later date. If such a proof is lacking, the properties of samples measured after storage cannot be used with confidence in the description of natural water. Reproducibility of measurements of properties of samples in the laboratory after sample storage cannot be used to prove that the sample represents the natural water, because they may be merely demonstrations that all such samples have reached a particular state (set of properties) and that state may not be the same as the natural state.

To facilitate the discussion of interactions between various substances, a phase is defined as a substance (liquid, gas, or solid) of fixed chemical potential for all components. A component is one of the necessary and sufficient chemical (compositional) variables to describe the compositions of all phases in a system. A constituent is a physically dependent compositional variable in that it cannot be varied at will without concomitant changes occurring. By the laws of electrostatics, for example, the concentration of an ion cannot be varied without inducing electrical potentials, or without a corresponding change in the concentrations of ions of the opposite sign. Species is the generic term including components and constituents.

The Gibbs free energy, G, is a fundamental thermodynamic property, and by use of the Gibbs free energy the necessary relations among the different types of reactions, compositions, and physical variables may be derived. There is no way of directly measuring G, and the absolute value of G is known only by definition. Changes in G can be determined by measurement of operational or experimental properties, such as electrochemical potentials, temperature, pressure, compositions, and the like. The dependence of G upon each of the operational variables used in this study will be considered separately in sequence and will lead to general relations.

The Gibbs free energy, G, is a state variable depending upon the temperature, pressure, and composition of the system as

$$G=G\left(T, P, \sum^{i} M_i\right), \tag{7}$$

where

T is the temperature,
P is the pressure, and
M_i is the amount of species i present.

Differentiating,

$$dG=\left(\frac{\partial G}{\partial T}\right)_{P,\, M_i, M_j \ldots} dT+\left(\frac{\partial G}{\partial P}\right)_{T,\, M_i, M_j \ldots} dP + \sum^{i}\left(\frac{\partial G}{\partial M_i}\right)_{T,\, P,\, M_j \ldots} dM_i \cdot \tag{8}$$

The Gibbs free energy may change with T, P, or composition. The change in G due only to composition changes is

$$dG=\sum^{i}\left(\frac{\partial G}{\partial M_i}\right)_{T,\, P,\, M_j} dM_i. \tag{9}$$

In the discussion of variation of G with composition, the partial derivatives have specified the change in concentration of a component or constituent without change in the composition of the phases. The physical process corresponding to the data analysis would be to use a sufficiently large sample such that no composition change would occur if the appropriate number of moles of a component were added. The free energy change from such a process is calculated and compared to the change if 1 mole—gram formula weight (GFW)—of the solid phase were added.

Consider the change in G if components such as a, b, c are added to the system containing phases I, J, K. Three phenomena may be observed. A component may be a solid and remain a solid (phase I), in which case, all other phases remaining constant,

$$dG=\left(\frac{\partial G_I}{\partial M_a}\right)_{T,\, P,\, M_J, M_K} dM_a; \tag{10}$$

or it may dissolve in a solid solution I also containing components b and c, in which case

$$dG=\left(\frac{\partial G_I}{\partial M_a}\right)_{M_b, M_c,\, M_J,\, M_K,\, T,\, P} dM_a; \tag{11}$$

or it may dissolve in an aqueous phase I producing changes in the concentration of a number of constituents i, all derived from component a, in which case the change is summed individually over all species i, j, derived from the solution of component a,

$$dG=\sum^{i}\left(\frac{\partial G_I}{\partial M_i}\right)_{T,\, P,\, M_j,\, M_K} dM_i. \tag{12}$$

Although the concepts remain unchanged, notation becomes simpler if the partial derivatives are defined as chemical potentials. For constituents in a solution I,

$$\mu_i \equiv \left(\frac{\partial G_I}{\partial M_i}\right)_{T,P,M_j}, \tag{13}$$

and for components,

$$\mu_a \equiv \left(\frac{\partial G_I}{\partial M_a}\right)_{T,P,M_b,M_c} \tag{14}$$

A rich variety exists for the expression of M, from such archaic units as grains per gallon (sometimes used for potable waters) to conveniences such as mole fractions (for solid solutions). The solids are considered here as invariant in composition for the sake of simplicity, although the assumption is not valid in detail. For aqueous solutions the specific variable M_i will be used, where m_i represents the moles per kilogram of solvent (water).

A criterion for equilibrium between two phases is that the chemical potential be the same for each component in both phases (Denbigh, 1955, p. 80–85). For equilibrium, then

$$(\mu_a)_I = (\mu_a)_J \tag{15}$$

In keeping with the usual conventions, the Gibbs free energy content of the elements in their stable form at 1 atmosphere pressure and 25° C (reference state) is zero,

$$G^{\circ}_{\text{elem, 25°C, 1 atm, stable form}} \equiv 0. \tag{16}$$

Generally, for pure components at a temperature of 25° C, 1 atm total pressure (standard state)

$$G^{\circ}_{25^{\circ},\,1\text{ atm}} \neq 0. \tag{17}$$

The reference state is a definition of the thermodynamic state, an arbitrary reference for subsequent work. The standard state, however, is merely a uniform set of conditions (pure component, at a temperature and pressure) chosen for the comparison of the free energies of the various components in different phases. For clarity, again, the process is to add a mole of solid to such a large amount of the solution studied that the composition of the solution-solid mixture remains unchanged. Under such conditions, for the solid,

$$\left(\frac{\partial G}{\partial M_i}\right)_{T,P,M_j} = \frac{G}{(\text{GFW})_i} = G_i^{\circ} = \mu_i^{\circ}. \tag{18}$$

For dissolved (aqueous) species the standard state used here, in keeping with standard practice, is an ideal 1 molal solution. An ideal solution is defined as one for which.

$$RT \ln m_i = \mu_i - \mu_i^{\circ}, \tag{19}$$

where R is the gas constant, so that for the ideal 1 molal solution, then,

$$RT \ln 1 = \mu_i - \mu_i^{\circ}, \tag{20}$$

or the chemical potential of the solute (μ_i) is the standard state chemical potential

$$\mu^{\circ}{}_i = \mu_i. \tag{21}$$

For the solutes in the standard state we can make the statement that

$$\left(\frac{\partial G}{\partial M_i}\right)_{T,P,M_j} = \frac{G}{(GFW)_i} = G_i^{0} = \mu_i^{0}. \tag{22}$$

Thus, Latimer's compilation of "free energies" is a compilation (Latimer, 1952) of molal free energies which are always numerically equal to and, if the experimental procedure is properly chosen, become identical to standard state chemical potentials. For an actual reaction such as

$$Cu_2S + 2H^+ = 2Cu^+ + H_2S_{(aq)} \tag{23}$$

the proportions among reactants and products are given by the coefficients for the species. The Gibbs free energy is an extensive variable and thus depends on the amount of material. Consequently, the molal free energies or chemical potentials must be considered in the proper proportions. The chemical potentials are summed over products and reactants, the general case being

$$\Delta G = \sum G_{\text{prod}} - \sum G_{\text{react}}, \tag{24}$$

or

$$\Delta\mu = \sum \mu_{\text{prod}} - \sum \mu_{\text{react}}. \tag{25}$$

For the reaction cited,

$$\Delta G = 2G_{Cu^+} + G_{H_2S_{(aq)}} - G_{Cu_2S} - 2G_{H^+} \tag{26}$$

and

$$\Delta\mu = 2\mu_{Cu^+} + \mu_{H_2S(aq)} - \mu_{Cu_2S} - 2\mu_{H}{}^{+}. \tag{27}$$

The condition for equilibrium is

$$\Delta G = \Delta\mu = 0. \tag{28}$$

The solid, if present in the real systems studied, should neither increase nor decrease in amount. There should be neither a net dissolution nor a net precipitation, although, of course, the solid may recrystallize. If

$$\Delta G = \Delta\mu > 0, \tag{29}$$

then the products of the reaction have a higher Gibbs free energy or a higher sum for the chemical potentials. The condition for a spontaneous reaction

$$\Delta G < 0 \tag{30}$$

may be met if the species on the left-hand side of the chemical equation (the "reactants") react to produce more of the species on the right. This is only a potential, however, and it cannot be inferred nor is it meant to be implied that such reactions indeed occur. Independent nonthermodynamic arguments must be supplied before the reaction can be shown to take place, even if large potentials exist to drive the reaction. The purpose of the present paper is to show such potentials that exist in real systems and then evidence to indicate what, if any, of the formal reactions considered do indeed occur.

In the tests for the states of reactions, the only unambiguous statement that can be made concerning solutions supersaturated with respect to a solid is that they are supersaturated. As a consequence, all that is known is that the sum of the chemical potentials of the postulated dissolved species is larger than the chemical potential of the solid.

Many methods may be used to compare states of reactions. A fundamental approach is by way of chemical potentials. Consider the reaction

$$\mathrm{Cu_2S+2H^+=2Cu^+ +H_2S_{(aq)}}. \qquad (31)$$

The changes in free energy may be written, in general,

$$\Delta G=2G_{\mathrm{Cu^+}}+G_{\mathrm{H_2S(aq)}}-G_{\mathrm{Cu_2S}}-2G_{\mathrm{H^+}}, \qquad (32)$$

for the standard state,

$$\Delta G^\circ=2G_{\mathrm{Cu^+}}{}^\circ+G_{\mathrm{H_2S(aq)}}{}^\circ-G_{\mathrm{Cu_2S}}{}^\circ-2G_{\mathrm{H^+}}{}^\circ, \qquad (33)$$

and for the equilibrium state involving solid pure $\mathrm{Cu_2S}$,

$$0=\Delta G'=2G_{\mathrm{Cu^+}}{}'+G_{\mathrm{H_2S(aq)}}{}'-G_{\mathrm{Cu_2S}}{}^\circ-2G_{\mathrm{H^+}}{}'. \qquad (34)$$

The equivalent arguments in terms of chemical potentials are, in general,

$$\Delta\mu=2\mu_{\mathrm{Cu^+}}+\mu_{\mathrm{H_2S(aq)}}-\mu_{\mathrm{Cu_2S}}{}^\circ-2\mu_{\mathrm{H^+}}, \qquad (35)$$

standard state,

$$\Delta\mu^\circ=2\mu_{\mathrm{Cu^+}}{}^\circ+\mu_{\mathrm{H_2S(aq)}}{}^\circ-\mu_{\mathrm{Cu_2S}}{}^\circ-2\mu_{\mathrm{H^+}}, \qquad (36)$$

and, at equilibrium, if pure solid $\mathrm{Cu_2S}$ be present,

$$0=2\mu_{\mathrm{Cu^+}}{}'+\mu_{\mathrm{H_2S(aq)}}{}'-\mu_{\mathrm{Cu_2S}}{}^\circ-2\mu_{\mathrm{H^+}}. \qquad (37)$$

Each of the equalities may be added or subtracted. For example, the standard state may be subtracted from the equilibrium state so that

$$0-\Delta\mu^\circ=2(\mu_{\mathrm{Cu^+}}{}'-\mu_{\mathrm{Cu^+}}{}^\circ)+(\mu_{\mathrm{H_2S(aq)}}{}'-\mu_{\mathrm{H_2S(aq)}}{}^\circ)$$
$$-(\mu_{\mathrm{Cu_2S}}{}'-\mu_{\mathrm{Cu_2S}}{}^\circ)-2(\mu_{\mathrm{H^+}}{}'-\mu_{\mathrm{H^+}}{}^\circ). \qquad (38)$$

For ideal solutions, by definition,

$$RT\ln m_i=(\mu_i-\mu_i{}^\circ). \qquad (39)$$

For real solutions

$$RT\ln \alpha_i=(\mu_i-\mu_i{}^\circ) \qquad (40)$$

where

$$\alpha_i=m_i\gamma_i. \qquad (41)$$

γ_i, the activity coefficient, is used to describe real solutions ($\gamma_i\neq 1$) in terms of ideal solutions ($\gamma_i=1$). γ_i is calculated from an extension of the Debye-Hückel limiting law. By substituting for $(\mu'_i-\mu^\circ_i)$ for the ideal solution postulated, if $\mathrm{Cu_2S}$ be present,

$$-\Delta\mu^\circ=2RT\ln m_{\mathrm{Cu^+}}+RT\ln m_{\mathrm{H_2S}}-RT\ln 1-2RT\ln m_{\mathrm{H}}{}^{+} \qquad (42)$$

and because

$$-\Delta\mu^\circ=-\Delta G^\circ \qquad (43)$$

the familiar formulation for ideal solutions may be derived

$$\Delta G^\circ=-RT\ln\frac{(m_{\mathrm{Cu^+}})^2(m_{\mathrm{H_2S}})}{1(m_{\mathrm{H^+}})^2}, \qquad (44)$$

and, of course, the expression

$$\frac{(m_{\mathrm{Cu^+}})^2(m_{\mathrm{H_2S}})}{1(m_{\mathrm{H^+}})^2} \qquad (45)$$

is the equilibrium constant K_1 assuming an ideal solution. For real solutions, if $\mathrm{Cu_2S}$ be assumed present, the same treatment yields

$$\Delta G^\circ=\Delta\mu^\circ=-RT\ln\frac{(\alpha_{\mathrm{Cu^+}})^2(\alpha_{\mathrm{H_2S}})}{1(\alpha_{\mathrm{H^+}})^2}. \qquad (46)$$

Thus far the properties of the equilibrium state for both ideal and real solutions have been developed, but both are special cases. The general case of real solutions can be obtained by adding the chemical potentials for any state to the standard state. So, for the reaction cited,

$$\Delta\mu-\Delta\mu^\circ=2(\mu_{\mathrm{Cu^+}}-\mu_{\mathrm{Cu^+}}{}^\circ)+(\mu_{\mathrm{H_2S}}-\mu_{\mathrm{H_2S}}{}^\circ)$$
$$-(\mu_{\mathrm{Cu_2S}}-\mu_{\mathrm{Cu_2S}}{}^\circ)-2(\mu_{\mathrm{H^+}}-\mu_{\mathrm{H^+}}{}^\circ). \qquad (47)$$

Upon substitution of

$$RT\ln\alpha_i=\mu_i-\mu_i{}^\circ \qquad (48)$$

the relation becomes

$$\Delta\mu-\Delta\mu^\circ=2RT\ln\alpha_{\mathrm{Cu^+}}+RT\ln\alpha_{\mathrm{H_2S}}-RT\ln\alpha_{\mathrm{Cu_2S}}$$
$$-2RT\ln\alpha_{\mathrm{H^+}}. \qquad (49)$$

Combining the last terms,

$$\Delta\mu-\Delta\mu^{\circ}=RT\ln\frac{(\alpha_{Cu^{+}})^{2}(\alpha_{H_2S})}{(\alpha_{Cu_2S})(\alpha_{H^{+}})^{2}}. \qquad (50)$$

The product

$$\frac{(\alpha_{Cu^{+}})^{2}(\alpha_{H_2S})}{(\alpha_{Cu_2S})(\alpha_{H^{+}})^{2}}. \qquad (51)$$

is defined as the activity product. At equilibrium the activity product (*AP*) is equal to the equilibrium constant, *K*. If

$$AP>K,$$

the solution is supersaturated, or if

$$AP<K,$$

the solution is unsaturated. If

$$AP=K,$$

then the solution is in equilibrium and

$$\Delta\mu=\Delta\mu'=0. \qquad (52)$$

The equations

$$\Delta\mu-\Delta\mu^{\circ}=RT\ln AP \qquad (53)$$

and

$$\Delta\mu^{\circ}=-RT\ln K \qquad (54)$$

may be added, and

$$\Delta\mu-\Delta\mu^{\circ}+\Delta\mu^{\circ}=RT\ln\frac{AP}{K} \qquad (55)$$

results in

$$\Delta\mu=RT\ln\frac{AP}{K}. \qquad (56)$$

The natural logarithm of the *AP*/*K* ratio times the gas constant and absolute temperature, then, gives a direct measure of the sum of the chemical potentials of species involved in the reaction, and hence gives a direct measure of the potential existing for the reaction under consideration. From the above considerations, only a sum of the chemical potentials may be determined, and only a ratio of *AP* to *K* for real solutions. The choice is entirely arbitrary as to which species is considered to be present in supersaturated or unsaturated concentration for solids which, barring solid solution or extremely fine grain size, may have only $\alpha=1$.

To be consistent and orderly in the presentation of the data, an entirely arbitrary decision was made to assign the excess (or deficiency) in the chemical potential entirely to the metallic cation in solution. Others for particular reasons may wish to assign the departures from equilibrium to the anion, hydrogen ion, or some other species. The hydrogen ion, being involved in most geochemical reactions, apparently merits special consideration in that nearly all departures from equilibrium could be expressed in a pH difference between actual and equilibrium states. Of course, to bring about a pH change some other species would have to be gained or lost from solution, and so the description of states solely in terms of pH differences may be misleading and obscure other and equally important consideration.

Having in hand methods for treating systems of varying composition, arguments for systems of varying physical properties are necessary. The differential

$$dG=\left(\frac{\partial G}{\partial P}\right)_{T,\,M_i,\,M_j\,\ldots}dP+\left(\frac{\partial G}{\partial T}\right)_{P,\,M_i,\,M_j\,\ldots}dT+\sum^{i}\left(\frac{\partial G}{\partial M_i}\right)_{T,\,P,\,M_j\,\ldots}dM_i \qquad (57)$$

will be simplified by assuming constant compositions for all phases of the systems discussed. For the constant composition case

$$dG=\left(\frac{\partial G}{\partial P}\right)_{T}dP+\left(\frac{\partial G}{\partial T}\right)_{P}dT. \qquad (58)$$

The significance of both $\left(\frac{\partial G}{\partial P}\right)_{T,\,M_i}$ and $\left(\frac{\partial G}{\partial T}\right)_{P,\,M_i}$ falls from the definition of *G*,

$$G=H-TS. \qquad (59)$$

For systems undergoing physical processes at a constant composition, by differentiation,

$$dG=dH-TdS-SdT, \qquad (60)$$

where
S is entropy and
H is the enthalpy, given by

$$dH=dU+PdV+VdP, \qquad (61)$$

where
V is the volume and
U is the internal energy and is given by

$$dU=dQ-dW, \qquad (62)$$

where
Q is the heat added to the system and
W is the work done by the system,

which is a statement of the law of conservation of energy (first law of thermodynamics). Upon substitution,

$$dG=dQ-dw+PdV+VdP-TdS-SdT. \qquad (63)$$

For reversible reactions

$$dQ=TdS. \qquad (64)$$

The work of expansion against a pressure (W_{exp}) may be expressed for constant pressure conditions as

$$dW_{exp}=PdV \tag{65}$$

For mass-action reactions the only work done is the work of expansion. Also, the equilibrium state is of interest as a reference.

Reversibility will be postulated for all reactions considered to calculate the properties of the equilibrium (reference), which will be compared to the actual states for the reactions. Postulating reversibility (which is to be tested), the dependence of G° on physical conditions reduces to

$$dG^\circ=PdV^\circ-S^\circ dT. \tag{66}$$

The aqueous solutions studied are nearly incompressible and, at the shallow depths found,

$$dV^\circ\approx 0. \tag{67}$$

The temperature dependence of G° is, then,

$$\frac{dG^\circ}{dT}=-S^\circ. \tag{68}$$

Substituting for $-S^\circ$,

$$\frac{dG^\circ}{dT}=\frac{G^\circ-H^\circ}{T}. \tag{69}$$

Dividing by T^2 and rearranging,

$$\frac{d\left(\frac{G^\circ}{T}\right)}{dT}=-\frac{H^\circ}{T^2}. \tag{70}$$

The equilibrium constant is related to G

$$RT\ln K=G^\circ \tag{71}$$

and so

$$\frac{d\ln K}{dT}=\frac{H^\circ}{RT^2}, \tag{72}$$

which is the van't Hoff equation which is used extensively in the data analysis to compute equilibrium states at the temperatures actually found in the field study.

In the treatment of electrochemical state the concern is with both chemical changes such as

$$Fe^{+2}\rightarrow Fe^{+3}, \tag{73}$$

and the concomitant physical changes as electrons are transferred as

$$Fe^{+2}=Fe^{+3}+e^{-}. \tag{74}$$

In consequence, the two common formulations must be combined. If in general

$$dG=\left(\frac{\partial G}{\partial P}\right)_{T,m_i}dP+\left(\frac{\partial G}{\partial T}\right)_{P,m_i}dT+\sum^{i}\left(\frac{\partial G}{\partial m_i}\right)_{T,P}dm_i, \tag{75}$$

and at fixed composition

$$dG=dH-TdS-SdT, \tag{76}$$

then

$$\left(\frac{\partial G}{\partial P}\right)_{T,m_i}dP+\left(\frac{\partial G}{\partial T}\right)_{P,m_i}dT=dH-TdS-SdT. \tag{77}$$

The Gibbs free energy change then may be stated as

$$dG=dH-TdS-SdT+\sum^{i}\left(\frac{\partial G}{\partial m_i}\right)dm_i. \tag{78}$$

Combining the definitions of internal energy and enthalpy with the free energy,

$$dG=dQ-dW+PdV+VdP-SdT-TdS+\sum^{i}\left(\frac{\partial G}{\partial m_i}\right)_{T,P}dm_i. \tag{79}$$

dQ and dW are dependent upon the path of any change occurring in the system of interest. If spontaneous changes occur there may also arise conditions for which dG may not be determined because of the uncertainty of state properties (P, T, V among others). The objective of the data analysis reported here is to determine states of solutions, some of which may react very slowly, if at all. Given the constancy of state—P, T, composition, Emf (electromotive force)—the thermodynamic properties of the systems may be defined. In the derivations of the functions of interest it will be assumed that the states of the solutions found were attained along reversible paths so that exact values of the properties may be obtained. For reversible paths

$$dQ=TdS. \tag{80}$$

The work of expansion against a confining pressure (work done) P is given by

$$dW_{exp}=PdV. \tag{81}$$

If the only work done by the system consists of electrical work done on the system, and the work of expansion, then

$$dG=+dW_{el}+VdP-SdT+\sum^{i}\left(\frac{\partial G}{\partial m_i}\right)_{T,P}dm_i. \tag{82}$$

If the system is held at a constant pressure and temperature ($dT=dP=0$) and the definition

$$\mu_i\equiv\left(\frac{\partial G}{\partial m_i}\right)_{P,T,M_i} \tag{83}$$

is used, then

$$dG = dW_{\mathrm{el}} + \sum^{i} \mu_i dm_i. \tag{84}$$

Returning to the example used, of

$$\mathrm{Fe}^{\circ} = \mathrm{Fe}^{+2} + 2e^{-}, \tag{85}$$

the free energy change for infinitesimal changes in the composition of the system is

$$\Delta\mu = \mu_{\mathrm{Fe}^{+2}} + 2\mu_{e^{-}} - \mu_{\mathrm{Fe}^{\circ}}. \tag{86}$$

In oxidizing one equivalent of Fe° to Fe^{+2}, a free energy change occurs. If one equivalent of Fe° is oxidized to Fe^{+2} in such a large amount of solution that the composition remains virtually unchanged, then, again, the identifications

$$\Delta\mu = \Delta G = \sum^{i} \mu = \sum^{i} G. \tag{87}$$

The problem with such a thought experiment is the very large increase in the electrical potential due to the accumulation of electrons. Guggenheim (1950, p. 330–412) gives an extended discussion of the point and shows there is no way of separating the individual μ_i values of the reaction. No experimental method exists for the measurement of $\mu_{\mathrm{Fe}^{+2}}$ independently of $\mu_{e^{-}}$ in the example given here. A convenient but entirely arbitrary convention is adopted here. The convention is

$$\mu_{e^{-}} \equiv 0, \tag{88}$$

from which, for the example cited,

$$\Delta\mu = \mu_{\mathrm{Fe}^{+2}} - \mu_{\mathrm{Fe}^{\circ}}. \tag{89}$$

The convention assigns all chemical potential differences to the chemical species and the electrons represent the resulting electrical charges. The sum of the charges over a reaction is the charge or quantity of electrical energy transferred in the course of the reaction.

If two half cells, one with an oxidizing reaction (yielding electrons) such as

$$\mathrm{Fe}^{\circ} \rightarrow \mathrm{Fe}^{+2} + 2e^{-} \tag{90}$$

and one with a reducing reaction (consuming electrons), such as the reaction to produce hydrogen gas, $\mathrm{H}_{2(\mathrm{g})}$,

$$2\mathrm{H}^{+} + 2e^{-} \rightarrow \mathrm{H}_{2(\mathrm{g})} \tag{91}$$

are connected in an electrical circuit, the charge transfer across the existing potential difference may be measured. Electrical work is the product of charge times the voltage difference. Along the conductors there is a demonstrably negligible change in the composition owing to electron flow. The law of conservation of energy, if obeyed, requires that the energy measured in the charge transfer be equal to the energy changes in the system. Along the conductor

$$dW_{\mathrm{el}} = E\,dQ, \tag{92}$$

where E is the electrical potential. In each half cell an identical energy change takes place as in the oxidation reaction

$$dG_{\mathrm{ox}} = \mu_{\mathrm{Fe}^{+2}} dm_{\mathrm{Fe}^{+2}} - \mu_{\mathrm{Fe}^{\circ}} dm_{\mathrm{Fe}^{\circ}} \tag{93}$$

and in the reduction reaction

$$dG_{\mathrm{red}} = \mu_{\mathrm{H}_{2(\mathrm{g})}} dm_{\mathrm{H}_{2(\mathrm{g})}} - \mu_{\mathrm{H}^{+}} dm_{\mathrm{H}^{+}}. \tag{94}$$

The energy yielded by one reaction is consumed in the other.

For one equivalent of electrons,

$$W_{\mathrm{el}} = E. \tag{95}$$

As with the hydrolysis reactions, the proportions of reactants and products must be considered, and if n electrons are produced or used in a reaction, then

$$W_{\mathrm{el}} = nE. \tag{96}$$

For each half cell, from the convention adopted,

$$dG_{\text{half cell}} = \sum^{i} \mu_i dm_i. \tag{97}$$

From the discussion thus far, it is possible to formulate useful functions for the description of the states of redox reactions in natural systems. For two half cells, such as

$$\mathrm{Fe}^{\circ} = \mathrm{Fe}^{+2} + 2e^{-} \tag{98}$$

and

$$2\mathrm{H}^{+} + 2e^{-} = \mathrm{H}_{2(\mathrm{g})}, \tag{99}$$

imagine a situation in which the electrodes (the electron acceptors from or donors to the solutions in the half cells) are in intimate contact with such a large amount of solution that allowing an integral number of moles to react will not change the composition of the solutions. Then the internal changes to the chemical system are

$$\Delta G_{\text{reaction}} = \sum G_{\text{products}} - \sum G_{\text{reactants}} = \sum \mu_{\text{products}} - \sum \mu_{\text{reactants}} \tag{100}$$

and the external changes (the electrical work measured on the electrical path)

$$\Delta G_{\text{conductor}} = nE\mathfrak{F} \tag{101}$$

where $\mathfrak{F}$ is the voltgram equivalent of the G units, so that

$$\Delta G_{\text{reaction}} = nE\mathfrak{F}. \tag{102}$$

$\Delta G_{\text{reaction}}$ is ambiguous, there being two reactions that must be coupled to preserve electrical neutrality. For clarity, the convention used is that for the reaction (half cell reactions will for brevity be referred to as reactions) in the state specified (the standard state)

$$H_{2(g,\,1\text{ atm},\,T)} = 2H^{+}{}_{(\alpha=1)} + 2e^{-} \tag{103}$$

$$\Delta G^{\circ} = 0 = 2E^{\circ}\mathfrak{F} \tag{104}$$

$$E^{\circ} = 0 \tag{105}$$

where E° is the potential for half cells in which all reactants and products are in their standard states.

For half cells measured against the hydrogen half cell, which is the reference half cell for all the subsequent discussion, the free energy change is merely the free energy change of the half cell. The total free energy change due to chemical reactions in the two half cells is

$$\Delta G = \left(\sum G_{\text{products}} - \sum G_{\text{reactants}}\right)_{\text{half cell}} + \left(\sum G_{\text{products}} - \sum G_{\text{reactants}}\right)_{\text{half cell}}, \tag{106}$$

and for the special case of a potential referred to a standard hydrogen half cell,

$$\Delta G = \left(\sum G_{\text{products}} - \sum G_{\text{reactants}}\right)_{\text{half cell}} - 0. \tag{107}$$

The relation between free energy and potential is

$$\Delta G = n\mathfrak{F}Eh \tag{108}$$

where Eh is the potential of the half cell as measured or referred to the standard hydrogen half cell. For reactions in which all reactants and products are in their standard states,

$$\Delta G^{\circ} = n\mathfrak{F}E^{\circ} \tag{109}$$

where E° is the standard electrode potential. The standard potentials are of course referred to the standard hydrogen half cell just as are all nonstandard potentials (Eh).

From an analogous argument to that used for the activity product, the relations among compositions of half cells, the chemical potentials, and electrical potentials may be derived. The case is slightly different because in the general case two reactions are considered, one in each half cell. For each half cell the reactants and products may be related to the standard state as

$$n\mathfrak{F}E^{\circ} = \sum^{i}\left(\mu_{i\,\text{products}}{}^{\circ} - \mu_{i\,\text{reactants}}{}^{\circ}\right) \tag{110}$$

and in general

$$n\mathfrak{F}Eh = \sum^{i}\left(\mu_{i\,\text{products}} - \mu_{i\,\text{reactants}}\right). \tag{111}$$

For the example chosen

$$Fe^{\circ} = Fe^{+2} + 2e^{-} \tag{112}$$

$$2\mathfrak{F}E^{\circ} = \mu_{Fe^{+2}}{}^{\circ} - \mu_{Fe^{\circ}}{}^{\circ}, \tag{113}$$

and in general

$$2\mathfrak{F}Eh = \mu_{Fe^{+2}} - \mu_{Fe^{\circ}}{}^{\circ}, \tag{114}$$

because the pure Fe metal is in its standard state (the stable modification at 1 atmosphere pressure). The equations may be subtracted to give, respectively, the general case referred to the standard hydrogen half cell

$$n\mathfrak{F}(Eh - E^{\circ}) = \sum^{i}(\mu_i - \mu_i{}^{\circ})_{\text{products}} - \sum^{i}(\mu_i - \mu_i{}^{\circ})_{\text{reactants}}, \tag{115}$$

and for the example used,

$$2\mathfrak{F}(Eh - E^{\circ}) = (\mu_{Fe^{+2}} - \mu_{Fe^{+2}}{}^{\circ}) - (\mu^{\circ}{}_{Fe^{\circ}} - \mu^{\circ}{}_{Fe^{\circ}}). \tag{116}$$

From the definition of the activity of a species,

$$RT \ln \alpha_i = \mu_i - \mu_i{}^{\circ} \tag{117}$$

the equations become

$$n\mathfrak{F}(Eh - E^{\circ}) = RT\left\{\sum^{i}(\ln \alpha_i)_{\text{products}} - \sum^{i}(\ln \alpha_i)_{\text{reactants}}\right\} \tag{118}$$

and

$$2\mathfrak{F}(Eh - E^{\circ}) = RT\{\ln \alpha_{Fe^{+2}} - \ln \alpha_{Fe^{\circ}}\}. \tag{119}$$

The transformation to the well-known Nernst equation follows directly as

$$Eh = E^{\circ} + \frac{RT}{n\mathfrak{F}} \ln \frac{(\alpha_i)_{\text{products}}}{(\alpha_i)_{\text{reactants}}} \tag{120}$$

and

$$Eh = E^{\circ} + \frac{RT}{2\mathfrak{F}} \ln \alpha_{Fe^{+2}}. \tag{121}$$

Because the iron metal is in its standard state

$$RT \ln \alpha_{Fe^{\circ}} = \mu^{\circ} - \mu^{\circ} = 0 \tag{122}$$

which can only be true if

$$\alpha_{Fe^{\circ}} = 1. \tag{123}$$

The form of the Nernst law given contains two conventions:

1. The departure of the state of the half cell from the standard state given by the term

$$\sum^{i}(\ln \alpha_i)_{\text{products}}-\sum^{i}(\ln \alpha_i)_{\text{reactants}}. \qquad (124)$$

2. The departure of the standard state from equilibrium with the standard hydrogen half cell given by the term E°.

Equations important in the analysis of the data reported in this paper fall from the derivations. First, from

$$n\mathfrak{F}(Eh-E^\circ)=\sum^{i}(\mu_i-\mu_i^\circ)_{\text{products}}-\sum^{i}(\mu_i-\mu_i^\circ)_{\text{reactants}}, \qquad (125)$$

$$n\mathfrak{F}Eh-n\mathfrak{F}E^\circ=\sum^{i}\mu_{i\,\text{products}}-\sum^{i}\mu_i{}^\circ{}_{\text{products}}-\sum^{i}\mu_{i\,\text{reactants}}+\sum^{i}\mu_i{}^\circ{}_{\text{reactants}}. \qquad (126)$$

Identifying

$$-n\mathfrak{F}E^\circ=-\sum^{i}\mu_i{}^\circ{}_{\text{products}}+\sum^{i}\mu_i{}^\circ{}_{\text{reactants}} \qquad (127)$$

it follows that

$$n\mathfrak{F}Eh=\sum^{i}\mu_{i\,\text{products}}-\sum^{i}\mu_{i\,\text{reactants}}. \qquad (128)$$

Alternatively put, because, by definition for the standard hydrogen half cell,

$$\Delta\mu^\circ=2\mu^\circ_{\text{H}^+}+2\mu^\circ_{e^-}-\mu_{\text{H}_2}\equiv 0, \qquad (129)$$

the sum of the chemical potentials over the half cell of interest,

$$\Delta\mu^*_i=\sum^{i}\mu_{i\,\text{products}}-\sum^{i}\mu_{i\,\text{reactants}}=n\mathfrak{F}Eh. \qquad (130)$$

$\Delta\mu^*_i$ does not constitute the difference between the equilibrium state of the half cell and the observed state of that half cell. Consistent with the theory developed in the section devoted to mass action reactions, $\Delta\mu_i$ is used for the chemical potential difference between observed states and equilibrium states. The nature of the $\Delta\mu^*_i$ for the half cell is quite different from the $\Delta\mu_i$ for the mass action reactions, such as hydrolysis, discussed earlier. The half cell reactions are compared to an external reference, and one necessary but not sufficient requirement for equilibrium between two half cells at the same T and P is that

$$(\Delta\mu^*_i)_a=(\Delta\mu^*_i)_b, \qquad (131)$$

or that

$$Eh_a=Eh_b. \qquad (132)$$

However, another requirement, independent of the first, is that all species be common to the two half cells and

$$(\mu_i)_a=(\mu_i)_b, \qquad (133)$$

from which, using the same standard state for species i in both half cells,

$$(\alpha_i)_a=(\alpha_i)_b. \qquad (134)$$

The criteria for equilibrium among the electrochemical reactions considered in the water are that the solutions have the same *Eh*, pH, and identical activities for all other species in addition to the hydrogen ion.

A last problem in the data analysis is the relation of the measured electrochemical properties to the values calculated for an equilibrium between various phases and the water. The problem is analogous to the relations among the chemical potentials, the activity products, and the equilibrium constants except for the additional complication of having to refer the electrochemical relations to an external standard, the standard hydrogen half cell.

In operational terms, the measuring device consists of an inert electrode (platinum) and an electrode of either known and fixed *Eh* or one having a constant *Eh* that can be measured (calibrated) in the field. The two electrodes may then be immersed in the water to be studied, and, taking appropriate precautions as discussed under "Methods of sampling and analysis," a measured *Eh* (Ehm) may be obtained. Experience has shown that the Ehm values may be reasonably uniform in time or, in other words, the measurements are reproducible. Early work also showed at least partial success in the interpretation of the Ehm in terms of states of chemical reactions of iron oxyhydroxides and oxides. In spite of the apparent success, in none of the work at any time have the specific reactions controlling the electrode potentials been known. The closest that one may come to such a knowledge is to find an agreement between the Ehm and an *Eh* calculated (EhTC) for a particular half cell at the temperature of the solution. It must be borne in mind that the agreement may be fortuitous or causal, and there is no way at present for distinguishing accidental agreement from the causal relation. The consistent results obtained earlier, along with those reported in this paper, indicate that the Ehm data obtained thus far are fundamental properties of the solutions studied and warrant further use in geochemical investigations. Put another way, the pH of a solution is a specific property that determines the behavior of a single species; the Ehm is a general property that cannot at present be related to a single specific reaction, but the Ehm must be used in the study of reactions involving electron transfer.

The analysis of the Ehm data may take several forms, as discussed in the section on "Data analysis." The concern here is the theoretical basis for the data analysis. In general, one of two cases may be found in the analysis of the Ehm data in terms of equilibrium with possible phases with the solution, or in terms of tests for an internal equilibrium distribution of dissolved species. The cases are the equilibrium case and the disequilibrium case. Taking the corrosion of iron, for example,

$$\mathrm{Fe}^{\circ}=\mathrm{Fe}^{+2}+2e-, \tag{135}$$

a value for EhTC may be calculated from

$$\mathrm{EhTC}=E^{\circ}{}_{(T)}+\frac{RT}{2\mathfrak{F}}\ln m_{\mathrm{Fe}^{+2}}\gamma_{\mathrm{Fe}^{+2}} \tag{136}$$

and compared to the Ehm value from observation. (Subscript obs indicates observed; calc indicates calculated.) If there is internal equilibrium, then

$$\mathrm{EhTC}=\mathrm{Ehm} \tag{137}$$

and

$$(\Delta\mu_i{}^{*})\ \mathrm{obs}=(\Delta\mu_i{}^{*})\ \mathrm{calc}. \tag{138}$$

At equilibrium, the difference in the chemical potentials between the actual and equilibrium states, $\Delta\mu_1$, is zero.

For the case in which

$$(\Delta\mu_i{}^{*})_{\mathrm{obs}}\neq(\Delta\mu_i{}^{*})_{\mathrm{calc}} \tag{139}$$

the departure from internal equilibrium can be put on the same formal basis as the departure from equilibrium in the mass action reactions.

The formulation falls readily out of the considerations above. The same convention is used also. The difference between $(\Delta\mu_i{}^{*})_{\mathrm{obs}}$ and $(\Delta\mu_i{}^{*})_{\mathrm{calc}}$ is arbitrarily assigned to the metal cation. Using the example of iron corrosion, Ehm can be used for the calculation of the equilibrium $\mu_{\mathrm{Fe}^{+2}}$ at the Ehm as

$$\mathrm{Fe}^{\circ}=\mathrm{Fe}^{+2}+2e^{-} \tag{140}$$

$$\mathrm{Ehm}=E_{(T)}{}^{\circ}+\frac{RT}{2\mathfrak{F}}\ln\left\{\frac{\alpha_{\mathrm{Fe}^{+2}\mathrm{eq}}}{\alpha_{\mathrm{Fe}^{\circ}}{}_{\mathrm{eq}}}\right\} \tag{141}$$

where the subscript eq would be the equilibrium value for appropriate species in the water of interest.

Alternatively, from

$$RT\ln\alpha_i=\mu_i-\overset{\circ}{\mu}_i, \tag{142}$$

$$RT\ln(\alpha_i)_{\mathrm{eq}}=(\mu_i)_{\mathrm{eq}}-\overset{\circ}{\mu}_i, \tag{143}$$

and

$$2\mathfrak{F}\ \mathrm{Ehm}-2\mathfrak{F}\ E^{\circ}_{(T)}=(\mu_{\mathrm{Fe}^{+2}}-\overset{\circ}{\mu}_{\mathrm{Fe}^{+2}})_{\mathrm{eq}}-(\mu_{\mathrm{Fe}^{\circ}}-\overset{\circ}{\mu}_{\mathrm{Fe}^{\circ}})_{\mathrm{eq}}. \tag{144}$$

The test for equilibrium tacitly assumes the phase of interest present; and, if the phase is solid and of only one component, then by definition

$$\mu_{\text{Solid phase}}\equiv\overset{\circ}{\mu}_{\text{Solid phase}}. \tag{145}$$

As a consequence

$$2\mathfrak{F}\ (\mathrm{Ehm}-E^{\circ}_{(T)})=(\mu_{\mathrm{Fe}^{+2}}-\overset{\circ}{\mu}_{\mathrm{Fe}^{+2}})_{\mathrm{eq}}. \tag{146}$$

More generally, for any reaction involving a solid,

$$n\mathfrak{F}\ (\mathrm{Ehm}-E^{\circ}_{(T)})=\sum^{i}(\mu_i-\mu_i{}^{\circ})_{\text{products, eq}}-\sum^{i}(\mu_i-\mu_i{}^{\circ})_{\text{reactants, eq}}=\Delta(\mu_i{}^{*})_{\mathrm{eq}}. \tag{147}$$

where the summation is over all species except the solid phase(s).

If

$$\Delta(\mu_i{}^{*})_{\mathrm{eq}}\neq\Delta(\mu_i{}^{*})_{\mathrm{obs}} \tag{148}$$

then a value for the *Eh* may be calculated from the actual composition of the sample, for example, for iron corrosion,

$$\mathrm{Fe}^{\circ}=\mathrm{Fe}^{+2}+2e^{-} \tag{149}$$

$$\mathrm{EhTC}=E^{\circ}_{(T)}+\frac{RT}{2\mathfrak{F}}\ln\left\{\frac{(\alpha_{\mathrm{Fe}^{+2}})_{\mathrm{obs}}}{(\alpha_{\mathrm{Fe}^{\circ}})_{\mathrm{obs}}}\right\}. \tag{150}$$

A treatment identical to the treatment of the equilibrium case leads to

$$2\mathfrak{F}(\mathrm{EhTC}-E^{\circ}{}_{(T)}=(\mu_{\mathrm{Fe}^{+2}}-\mu^{\circ}{}_{\mathrm{Fe}^{+2}})_{\mathrm{obs}} \tag{151}$$

or, in general,

$$n\mathfrak{F}(\mathrm{EhTC}-\mathrm{E}^{\circ}{}_{(T)})=\sum^{i}(\mu_i-\mu_i{}^{\circ})_{\text{products, obs}}-\sum^{i}(\mu_i-\mu_i{}^{\circ})_{\text{reactants, obs}}. \tag{152}$$

Subtracting the equilibrium state from the actual state

$$\begin{aligned}n\mathfrak{F}(\mathrm{EhTC}-E_{(T)}{}^{\circ})-n\mathfrak{F}(\mathrm{Ehm}-E_{(T)}{}^{\circ})&=\sum^{i}(\mu_i-\mu_i{}^{\circ})_{\text{products, obs}}\\&-\sum^{i}(\mu_i-\mu_i{}^{\circ})_{\text{reactants, obs}}\\&-\sum^{i}(\mu_i-\mu_i{}^{\circ})_{\text{products, eq}}\\&+\sum^{i}(\mu_i-\mu_i{}^{\circ})_{\text{reactants, eq}}\end{aligned} \tag{153}$$

and simplifying

$$\begin{aligned} n\mathfrak{F}(\mathrm{EhTC}-\mathrm{Ehm}) = & \sum^{i}(\mu_i)_{\mathrm{products,\ obs}} - \sum^{i}(\mu_i)_{\mathrm{reactants,\ obs}} \\ & - \sum^{i}(\mu_i)_{\mathrm{products,\ eq}} + \sum^{i}(\mu_i)_{\mathrm{reactants,\ eq}} \\ & - \sum^{i}(\mu_i{}^{\circ})_{\mathrm{products,\ obs}} + \sum^{i}(\mu_i{}^{\circ})_{\mathrm{reactants,\ obs}} \\ & + \sum^{i}(\mu_i{}^{\circ})_{\mathrm{products,\ eq}} - \sum^{i}(\mu_i{}^{\circ})_{\mathrm{reactants,\ eq}}. \end{aligned} \tag{154}$$

In the calculations, the identical species are considered and hence, under the same physical conditions, using the same reference state,

$$\sum^{i}(\mu_i{}^{\circ})_{\mathrm{obs}} \equiv \sum^{i}(\mu_i{}^{\circ})_{\mathrm{eq}} \tag{155}$$

and hence,

$$\begin{aligned} n\mathfrak{F}(\mathrm{EhTC}-\mathrm{Ehm}) = & \left(\sum^{i}(\mu_i)_{\mathrm{obs}} - \sum^{i}(\mu_i)_{\mathrm{eq}}\right)_{\mathrm{products}} \\ & - \left(\sum^{i}(\mu_i)_{\mathrm{obs}} - \sum^{i}(\mu_i)_{\mathrm{eq}}\right)_{\mathrm{reactants}} \equiv \Delta\mu_i. \end{aligned} \tag{156}$$

Care must be used in the interpretation of the potentials calculated and measured and of the relation between them. If, as may be found,

$$\mathrm{EhTC} \neq \mathrm{Ehm}, \tag{157}$$

then it may be immediately concluded that Ehm is not controlled by the particular reaction under study, and the inference is drawn that the reaction is insufficiently rapid to control the Ehm of the solution. The equilibrium state is indicated by the Ehm and sums of the μ_i's for each of the reactions. A seeming alternative explanation for differences between an EhTC value and the Ehm is that, for the particular reaction, the rate is so slow that the reaction does not control the composition of the solution. In fact, both the conclusions are the same; that is, if EhTC$\neq$Ehm, then the reaction is slow in comparison to the reaction(s) which do control the Ehm and is also too slow to affect the solution composition over as short a period of time as the measurement required. More fundamentally, the Nernst law gives the functional relationship between potential and composition and either or both may be chosen as the independent variable(s).

The variable $\Delta\mu_i$ has exactly the same significance in redox considerations as in mass-action considerations. It represents the difference in the chemical potential summed over the reaction as it actually is, less the equilibrium value, and gives the existing potential to drive the reaction. If more than one species is involved, as often happens, the assignment of the departure from equilibrium to any single species is arbitrary and without thermodynamic justification. The laws of electrostatics, from which the law of electrical neutrality is derived, forbid the addition or subtraction of a single charged species without corresponding large electrical potentials. If the disequilibrium state changes toward an equilibrium, the change cannot be by changing the activity of a single ion without concomitant changes. The path to equilibrium may be complicated if the activity of an ion involved in the reaction is varied (coupled with a nonreacting ion of opposite charge, in keeping with the requirement of electrical neutrality) because hydrolysis in the solution may bring about a change in the activities of some or all of the other reacting species.

For those more familiar with concentration data or activity data, however, the departures from equilibrium are also calculated in concentration and activity terms, and to the metal ion is assigned the whole value of $\Delta\mu$. Equilibrium concentrations of the metal ion are calculated keeping all other μ_i's constant. This is an entirely arbitrary convention and does not state how any system will change, but is offered as a convenient mode of expression of the fundamental properties in terms of familiar operational variables.

DATA ANALYSIS

Given the constituents found in the water, the solubilities of possible phases for which free energy data are available were calculated. The reactions used are strictly formal. They do not necessarily indicate a reaction mechanism or path.

The data analysis is broken into parts as follows:

1. Corrections for nonideal behavior of measuring systems.
2. Distributions of chemical species from the properties of the solutions.
3. Tests for the apparent behavior of the possible solids from available free energy data.

The pH data from field observations must be corrected to true data, and this was done using the procedures of Barnes (1964), including the measurement of the observed pH of two buffers.

Practical experience has shown that there may be discordance among saturated calomel electrode (SCE) potentials when measured against one another. Experience also has shown that the potential of a single SCE varies not only with temperature but with its history. The problem is not great in measuring pH because the potential of the SCE is opposed in the calibration of glass electrode-SCE pairs. In *Eh* measurement, however, an absolute Emf for the SCE is required, not merely a constant Emf. The solution cited by Garrels (1960, p. 168) and his temperature compensation functions were used to obtain absolute values of the *Eh* of the SCE. All measurements in the field were so calibrated where possible. For other field studies, Garrels' function (1960, p. 67) for the Emf of the SCE as a function of temperature was verified experimentally and used.

The second step in the data analysis is prone to more uncertainty than the problems of correcting observation to true values. The distribution of species perforce assumes equilibrium distributions of species in the aqueous phase. Hem (1963a) gives stability constants for ion pairs formed between Mn^{+2} and HCO_3^- and Mn^{+2} and SO_4^{-2}. Using Hem's constants, the actual concentration of Mn^{+2} (molal) is given by

$$m_{\mathrm{Mn}^{+2}}=\frac{m_{\mathrm{Mn\ TOT}}}{(1+190\times\gamma_{\mathrm{Mn}^{+2}}\times\alpha_{\mathrm{SO}_4^{-2}}+63\times\gamma_{\mathrm{Mn}^{+2}}\times m_{\mathrm{HCO}_3^-})} \tag{158}$$

where

$m_{\mathrm{Mn\ TOT}}$ is the total molality of Mn^{+2} by analysis,
$\gamma_{\mathrm{Mn}^{+2}}$ is the activity coefficient for Mn^{+2},
$\alpha_{\mathrm{SO}_4^{+2}}$ is the product of the molality of SO_4^{-2} times the activity coefficient of SO_4^{-2}, and
$m_{\mathrm{HCO}_3^-}$ is the molality of the HCO_3^- as reported by analysis.

Tacit in the above calculation is not only the equilibrium among the Mn species but also the presumed validity of individual ion activity coefficients. The question of the validity of individual ion activity coefficients has been argued for some years in the chemical literature. Many formulas have been proposed and their relative merits discussed. For details the reader is referred to Harned and Owen (1958), Robinson and Stokes (1959), and Guggenheim (1950). Both the rigor and accuracy of any formula used may be debatable. In dealing with naturally occurring solutions, however, which are invariably mixed electrolytes of widely ranging compositions, some model must be selected. The choice is arbitrary but made with the belief that a consistent and clearly defined treatment is to be preferred. The lack of data on individual or mean ion activity coefficients in the solutions studied and the impossibility of obtaining such data in the study here reported preclude an empirical check on the validity of the argument used. However, it seems safe to assume the activity coefficients calculated here are not more than one order of magnitude in error, and even an error of this magnitude would not vitiate the conclusions reached by the current data analysis.

The formula used for the computation of individual ion activity coefficient is:

$$-\ln\gamma_i=\frac{A^*d_w^{1/2}(DT)^{-3/2}z_i^2\,\Gamma^{1/2}}{1+a_oB^*d_w^{1/2}(DT)^{-1/2}\,\Gamma^{1/2}} \tag{159}$$

where

γ_i is the ion activity coefficient of the *i*th ion,
A^* is a constant involving only fundamental constants,
B^* is a constant involving only fundamental constants,
d_w is the density of pure water,
D is the dielectric constant of pure water,
T is the temperature in degrees centigrade,
Γ is the ionic strength,
z_i is the charge of the *i*th ion, and
a_o is the distance of nearest approach of solutes (Kielland, 1937).

$$\Gamma=\tfrac{1}{2}\sum^{i}m_i(z_i)^2 \tag{160}$$

where m_i is the molality of the *i*th ion; A^* and B^* are, respectively,

$$A^*=\left(\frac{e^3}{2.303k}\right)\left(\frac{2\pi N}{1000k}\right)^{1/2} \tag{161}$$

$$B^*=\left(\frac{8\pi e^2N}{1000k}\right)^{1/2} \tag{162}$$

where

e is the electronic charge,
N is Avogadro's number, and
k is Boltzmann's constant.

Values of A^* and B^* have been calculated from the values cited in the U.S. National Bureau of Standards (1963) and are:

$$A^*=1824347.0$$

$$B^*=50.297670$$

The density of water has been calculated from the function of Keenan and Keyes (1936, p. 21). The dielectric constant of water is calculated from the equation given by Jeffries Wyman and E. N. Ingalls as cited by Harned and Owen (1958, p. 159) up to 100° C. For flexibility not required for the studies reported here, the program listed in "Appendix 1" of this report gives the dielectric constant for the water-vapor saturated conditions from 100° C up to 360° C from the function of Akerlof and Oshry (1950).

The distribution of manganese species as cited above is simple in comparison to the distribution of copper species in solution. The pertinent reactions are:

$$Cu^+=Cu^{+2}+e^-, \tag{163}$$

$$2Cu^{+2}+2H_2O=Cu_2(OH)_2^{+2}+2H^+, \tag{164}$$

and

$$Cu_{\mathrm{TOT}}=Cu^{+2}+Cu^{+1}+2Cu_2(OH)_2^{+2}. \tag{165}$$

The equations may be solved readily for the distribution of copper. For example, a solution would be

$$(2m_{Cu^{+1}})^2\left\{\frac{\gamma_{Cu^{+1}}{}^2\alpha_{H_2O}{}^2}{\gamma_{Cu_2(OH)_2{}^{+2}}}(\alpha_{H^+})^{-2}E^{\frac{2\mathfrak{F}}{RT}(\mathrm{Ehm}\text{-}E_{12}°)}\right\}$$

$$+m_{Cu^{+1}}\left\{\frac{\gamma_{Cu^{+1}}}{\gamma_{Cu^{+2}}}E^{\frac{\mathfrak{F}}{RT}(\mathrm{Ehm}\text{-}E_{11}°}\right\}+m_{Cu^{+1}}=\mathrm{Cu_{TOT}} \qquad (166)$$

where

m is molality of the appropriate ion,
α is the activity of the appropriate ion,
$\mathfrak{F}$ is the volt gram formula weight equivalent,
R is the gas constant,
Ehm is the measured redox potential,
$E_{12}°$ is the standard state potential for the reaction

$$2Cu^{+1}+2H_2O=Cu_2(OH)_2{}^{+2}+2H^++2e^-, \qquad (167)$$

$E_{11}°$ is the standard state potential for the reaction

$$Cu^{+1}=Cu^{+2}+e^-, \text{ and} \qquad (168)$$

$\mathrm{Cu_{TOT}}$ is the total molality of copper species.

The function is a simple quadratic and, although cumbersome, would not be intractable except that

$$\left[\frac{\gamma_{Cu^{+1}}}{\gamma_{Cu^{+2}}}E^{\frac{\mathfrak{F}}{RT}(\mathrm{Ehm}-E_{11}°)}+1\right]^2>>4\left\{\left[2\frac{\gamma_{Cu^{+1}}{}^2\alpha_{H_2O}{}^2}{\gamma_{Cu_2(OH)_2{}^{+2}}}(\alpha_{H^+})^{-2}\right]\times E^{\frac{2\mathfrak{F}}{RT}(\mathrm{Ehm}-E_{12}°)}\right\}\mathrm{Cu_{TOT}}. \qquad (169)$$

In all three actual solutions examined as test cases for copper speciation, the exact solution would require accuracy to more than two significant figures for the copper analysis, but the analysis is not reliable to more than two significant figures. Several alternate methods of distributing copper species were tried. The one selected has the virtue of working and, although it requires significant programming, it is efficient in use of computer time and becomes increasingly efficient as any one of the species considered diminishes in importance. Again, it should be remembered that the speciation assumes an equilibrium distribution of dissolved species and valid ion activity coefficients.

As other copper species become important in other natural solutions, the data analysis will become more complex. The selection of Cu^+, Cu^{+2}, and $Cu_2(OH)_2{}^{+2}$ was made after preliminary calculations showed other species less important.

The distribution of sulfide species was based on an analysis of the data presented by Wright and Maas (1932). The data of Wright and Maas are still considered the most reliable obtained as a function of temperature. For the pH values of natural waters the reaction is

$$H_2S_{(aq)}=H^++HS^-. \qquad (170)$$

The results of Himmelblau and Loy (1961) are suspect because, in the dilute solutions they chose, adsorbed oxygen on their apparatus would pose serious problems. Two sets of finite difference calculations for $\Delta H°$ from Wright and Maas' data gave erratic results. A smooth curve was drawn through their data and the slope-normal method described by Swartzendruber and Olson (1963) was applied to obtain $\Delta H°$. From the $\Delta H°$ data obtained by the slope-normal method ΔC_p (the heat capacity differences at constant pressure) was calculated. The resulting equations are:

$$\Delta C_P=-0.0724454 \text{ kcal per mole (kilo calorie per mole)}, \qquad (171)$$

$$\Delta H°=-0.0724454\ T+27.4746 \text{ kcal per mole}, \qquad (172)$$

$$\log K=-36.456001 \log T-6.003400\times 10^3\left(\frac{1}{T}\right)+103.366829. \qquad (173)$$

Many more significant figures are carried than justified by the original data. It should be remembered that digital computers commonly carry 12 digits so that the best values of the functions are given to avoid rounding errors in extensive computation.

The tests for the behavior of each solid considered rely on the data of Latimer (1952), Garrels (1960), and Larson and Buswell (1942). The chemical reactions that are considered (and, again, are formal, using directly measured variables where possible) are:

Computer program reaction Nos.	*Hydrolysis reactions*	
0----	Cuprite: $Cu_2O+2H^+=2Cu^++H_2O.$	(174)
1----	Tenorite: $CuO+2H^+=Cu^{+2}+H_2O.$	(175)
2----	Copperhydroxide (no mineral name): $Cu(OH)_2+2H^+=Cu^{+2}+2H_2O.$	(176)
3----	Azurite: $Cu_3(CO_3)_2(OH)_2+2H^+=3Cu^{+2}+2CO_3{}^{-2}+2H_2O.$	(177)
4----	Malachite: $Cu_2(OH)_2CO_3+2H^+=2Cu^{+2}+CO_3{}^{-2}+2H_2O.$	(178)
5----	Covellite: $CuS+2H^+=Cu^{+2}+H_2S_{(aq)}.$	(179)
6----	Chalcocite: $Cu_2S+2H^+=2Cu^++H_2S_{(aq)}$	(180)
7----	Rhodochrosite: $MnCO_3=Mn^{+2}+CO_3{}^{-2}.$	(181)
8----	Ferrous hydroxide (no mineral name): $Fe(OH)_2+2H^+=Fe^{+2}+2H_2O.$	(182)
9----	Siderite: $FeCO_3=Fe^{+2}+CO_3{}^{-2}.$	(183)
10---	Magnesite: $MgCO_3=Mg^{+2}+CO_3{}^{-2}.$	(184)

Computer program reaction Nos. *Hydrolysis reactions*

11--- Dolomite:
$\mathrm{CaMg(CO_3)_2=Ca^{+2}+Mg^{+2}+2CO_3^{-2}}.$ (185)
12--- Calcite:
$\mathrm{CaCO_3=Ca^{+2}+CO_3^{-2}}.$ (186)
13--- Mackinawite:
$\mathrm{FeS+2H^+=Fe^{+2}+H_2S_{(aq)}}.$ (187)
14--- Chalcopyrite:
$\mathrm{CuFeS_2+4H^+=Cu^{+2}+Fe^{+2}+2H_2S_{(aq)}}.$ (188)
15--- Bornite:
$\mathrm{Cu_5FeS_4+8H^+=4Cu^++Cu^{+2}+Fe^{+2}+4H_2S_{(aq)}}.$ (189)
16--- Manganous hydroxide (no mineral name):
$\mathrm{Mn(OH)_2+2H^+=Mn^{+2}+2H_2O}.$
17--- Anhydrite:
$\mathrm{CaSO_4=Ca^{+2}+SO_4^{-2}}.$
18--- Gypsum:
$\mathrm{CaSO_4\cdot 2H_2O=Ca^{+2}+SO_4^{-2}+2H_2O}.$

Computer program reaction Nos. *Redox reactions*

0---- Iron:
$\mathrm{Fe=Fe^{+2}+2}e^-.$ (190)
1---- Magnetite:
$\mathrm{3Fe^{+2}+4H_2O=Fe_3O_4+8H^++2}e^-.$ (191)
2---- Ferric hydroxide (most soluble form of limonite):
$\mathrm{Fe^{+2}+3H_2O=Fe(OH)_3+3H^+}+e^-.$ (192)
3---- Hydrogen sulfide:
$\mathrm{H_2S_{(aq)}+4H_2O=SO_4^{-2}+10H^++8}e^-.$ (193)
4---- Pyrolusite:
$\mathrm{Mn^{+2}+2H_2O=MnO_2+4H^++2}e^-.$ (194)
5---- Hausmannite:
$\mathrm{3Mn^{+2}+4H_2O=Mn_3O_4+8H^++2}e^-.$ (195)
6---- Bixbyite:
$\mathrm{2Mn^{+2}+3H_2O=Mn_2O_3+6H^++2}e^-.$ (196)
7---- Pyrite:
$\mathrm{Fe^{+2}+2H_2S_{(aq)}=FeS_2+4H^++2}e^-.$ (197)
8---- Copper:
$\mathrm{Cu=Cu^{+2}+2}e^-.$ (198)
9---- Hematite (least soluble form of limonite):
$\mathrm{2Fe^{+2}+3H_2O=Fe_2O_3+6H^++2}e^-.$ (199)
10--- Pyrite:
$\mathrm{FeS_2+8H_2O=Fe^{+2}+2SO_4^{-2}+16H^++14}e^-.$ (200)
11--- Used to distribute copper species:
$\mathrm{Cu^+=Cu^{+2}}+e^-.$ (201)
12--- Used to distribute copper species:
$\mathrm{2Cu^++2H_2O=Cu_2(OH)_2^{+2}+2H^++2}e^-.$ (202)
13--- Manganic hydroxide (no mineral name):
$\mathrm{Mn^{+2}+3H_2O=Mn(OH)_3+3H^+}+e^-.$ (203)

For the hydrolysis reactions the equilibrium constants were calculated as a function of temperature if data were available. For calcite the function used is a least squares function fitted to the measurements of Larson and Buswell (1942) and is:

$$\ln K_{\mathrm{C}(T)}=27.8459347-8.257873\ln T \tag{204}$$

where $K_{C(T)}$ is the equilibrium constant of calcite in the form

$$K_{\mathrm{C}(T)}=\alpha_{\mathrm{Ca^{+2}}}\alpha_{\mathrm{CO_3^{-2}}}. \tag{205}$$

For the other hydrolysis reactions for which the standard state enthalpy ($\Delta H°$) only is known, the equation:

$$\ln K_{(T)}=\ln K_{298.15}-\frac{\Delta H°}{R}\left(\frac{1}{T}-\frac{1}{298.15}\right) \tag{206}$$

where

$K_{(T)}$ is the appropriate equilibrium constant in the form consistent with the hydrolysis reactions given, and

$K_{298.15}$ is the equilibrium constant at 25°C.

The tacit assumption that $\Delta C_p=0$ is used. For the azurite and malachite reactions not even $\Delta H°$ is known, so that the equilibrium constant is assumed independent of temperature or

$$\ln K_{(T)}=\ln K_{(298.15)}, \tag{207}$$

which is the same as assuming

$$\Delta H°=0.$$

The calculations for the temperature dependence of solubility are, in decreasing order of reliability:

1. From experimental data over a temperature range.
2. From experimental data including $\Delta H°$ at one temperature.
3. From solubility data at one temperature with no $\Delta H°$ data.

The equilibrium constants obtained by computation were combined with the activity product (AP) values from the observed composition of the water to give

$$\Delta\mu_{\mathrm{R}}=RT\ln\frac{AP}{K}. \tag{208}$$

The chemical potential existing because of the differences between actual and equilibrium states hence can be calculated for the hydrolysis reactions. Although, as pointed out in the theoretical discussion, there is no thermodynamic rigor in assigning departures from equilibrium to any single ion, it is a helpful index for those used to compositional variables. The convention used in this paper is consistent for all solids. The state of the reaction is expressed as a ratio of the actual activity of the metal cation divided by the activity of the metal cation at equilibrium. For example, for the reaction involving solid $\mathrm{Cu_2S}$

$$\mathrm{Cu_2S+2H^+=2Cu^++H_2S_{(aq)}}, \tag{209}$$

$$AP=\frac{(\alpha_{\mathrm{Cu^{+2}}})^2_{\mathrm{actual}}(\alpha_{\mathrm{H_2S(aq)}})_{\mathrm{actual}}}{(\alpha_{\mathrm{H^+}})^2_{\mathrm{actual}}}, \tag{210}$$

and

$$K=\frac{(\alpha_{\mathrm{Cu^{+2}}})^2_{\mathrm{eq}}(\alpha_{\mathrm{H_2S(aq)}})_{\mathrm{eq}}}{(\alpha_{\mathrm{H^+}})^2_{\mathrm{eq}}}. \tag{211}$$

If it is assumed that

$$(\alpha_{H_2S(aq)})_{\text{actual}}=(\alpha_{H_2S(aq)})_{\text{eq}} \tag{212}$$

and

$$(\alpha_{H^+})_{\text{actual}}=(\alpha_{H^+})_{\text{eq}}, \tag{213}$$

then

$$\frac{AP}{K}=\frac{(\alpha_{Cu^+})^2{}_{\text{actual}}}{(\alpha_{Cu^+})^2{}_{\text{eq}}} \tag{214}$$

and

$$\left(\frac{AP}{K}\right)^{1/2}=\frac{(\alpha_{Cu^+})_{\text{actual}}}{(\alpha_{Cu^+})_{\text{eq}}}. \tag{215}$$

If the assumption is made that

$$(\gamma_{Cu^+})_{\text{actual}}=(\gamma_{Cu^+})_{\text{eq}}, \tag{216}$$

then

$$\left(\frac{AP}{K}\right)^{1/2}=\frac{(m_{Cu^+})_{\text{actual}}}{(m_{Cu^+})_{\text{eq}}}=\text{CR}, \tag{217}$$

where CR is the cation ratio.

It is thus possible to arrive at a description of the state of a reaction in terms of concentration ratios or activity ratios in terms of single ions. The description is entirely arbitrary, however convenient it may seem to be. A rigorous comparison can be made, as has been shown, as

$$\Delta\mu_R=RT\ln\left(\frac{AP}{K}\right). \tag{218}$$

The data analysis for reactions involving electron transfer is only slightly more complicated than that for simple hydrolysis reactions. For example, for the reaction

$$\text{Fe}^\circ=\text{Fe}^{+2}+2e^-, \tag{219}$$

the Nernst law relation is

$$Eh_{(T)}=E_{(T)}{}^\circ+\frac{RT}{2\mathfrak{F}}\ln \alpha_{Fe^{+2}}. \tag{220}$$

For solutions at temperatures other than 25° C, the temperature variation of $E_{(T)}{}^\circ$ must be calculated. The function used is an integrated form of the Gibbs-Helmholtz equation and is

$$E_{(T)}{}^\circ=\frac{T}{298.15}E_{298.15}{}^\circ+\frac{\Delta H^\circ}{n\mathfrak{F}}\left(\frac{298.15-T}{298.15}\right), \tag{221}$$

implicit in which is the assumption

$$\Delta C_p=0. \tag{222}$$

Data on the temperature dependence of E° values are sorely lacking.

The chemical analysis and field study provide measured oxidation potentials (Ehm), T, and $m_{Fe^{+2}}$. Calculation of the individual ion activity coefficients such as $\gamma_{Fe^{+2}}$ make the Nernst equation determinate for two conditions, the actual state and the state for equilibrium. For example, from the measured oxidation potential the $\alpha_{Fe^{+2}}$ at equilibrium with iron metal may be calaculated as

$$\text{Ehm}=E_{(T)}{}^\circ+\frac{RT}{2\mathfrak{F}}\ln(\alpha_{Fe^{+2}})_{\text{eq}}. \tag{223}$$

From the measured $m_{Fe^{+2}}$ the oxidation potential that should be measured if the solution were in equilibrium with Fe° may be calculated as

$$\text{EhTC}=E_T{}^\circ+\frac{RT}{n\mathfrak{F}}\ln m_{Fe^{+2}}\gamma_{Fe^{+2}}. \tag{224}$$

The $(\alpha_{Fe^{+2}})_{\text{eq}}$ may be calculated from

$$(\alpha_{Fe^{+2}})_{\text{eq}}=e^{\frac{2\mathfrak{F}}{RT}(\text{Ehm}-E_T{}^\circ)}. \tag{225}$$

If

$$(\gamma_{Fe^{+2}})_{\text{eq}}=(\gamma_{Fe^{+2}})_{\text{actual}}, \tag{226}$$

then

$$\frac{(m_{Fe^{+2}})_{\text{actual}}}{(m_{Fe^{+2}})_{\text{eq}}}=\text{CR}, \tag{227}$$

which is in the same form as the CR for the hydrolysis reaction. The ratio of the activities, of course, would be numerically the same and be

$$\frac{(m_{Fe^{+2}})_{\text{actual}}(\gamma_{Fe^{+2}})_{\text{actual}}}{(\alpha_{Fe^{+2}})_{\text{eq}}}=\text{CR}. \tag{228}$$

The rigorous relation developed in the section on theory is

$$\Delta\mu_R=n\mathfrak{F}(\text{EhTC}-\text{Ehm}). \tag{229}$$

All the above ways of describing the states of the reactions studied have been used in the program given in the appendix.

RESULTS

For a completely rigorous treatment of solute species and the related apparent behavior of solid phases occurring in natural systems, it seems necessary to show the following:

1. The aqueous phase is supersaturated with a solid phase and the solid phase is precipitating.
2. The aqueous phase is supersaturated with a solid phase and the solid phase is not precipitating.

3. The aqueous phase is unsaturated with a solid phase and the solid phase is dissolving.
4. The aqueous phase is unsaturated with a solid phase and the solid phase is not dissolving.
5. An equilibrium exists between the aqueous phase and the solid phase.

If the information listed were available, then plausible reaction mechanisms could be postulated if sufficiently detailed information were available on the aqueous phase. If the time dependence of the precipitation or solution reactions, coupled with the concentrations (or activities) of the aqueous species were known, then kinetic interpretations could be made. Unfortunately, such information is not currently available.

Suppose that a solid phase is present in the natural system and that the aqueous phase is unsaturated with that solid. The only sure test of dissolution of the solid phase is by an artificial introduction of a known mass of that phase and by a measurement of the mass in time, assuming that the properties of the aqueous phase remain constant. In the present study, the only solid phase introduced into the wells (except for the corrosion probes) is iron metal, which is of slight geologic significance. Tests for the behavior of other solids with which the aqueous phase is possibly unsaturated are empty, in that their presence has not been established, and it cannot be proven that they do dissolve or do not dissolve.

The only tests available with present data relate to degree of departure from equilibrium of the solutions sampled at the wellhead with respect to appropriate solid phases, and a comparison with solids observed on well casing or screen in one well. Geologically, the nature of the substrate on which deposits are formed is probably of importance, but an assessment of the importance of the substrate cannot be made at this time. A further precaution is that, locally, solutions may be supersaturated or unsaturated, but the mixture of locally derived solutions as sampled at the wellhead may be quite different in its properties from each of the individual solutions.

In the extreme, the characterization of the apparent behavior of solid phases can be made only on the grounds of relative supersaturations, or departures from equilibrium. Presumably, if a phase is precipitating locally from a solution, perhaps not represented by the solution sampled at the wellhead, then broad limits for the behavior of possible solids may be inferred. At least the properties of an aqueous solution at the wellhead may be determined; and, in terms of the bulk or integrated sample, the behavior of various solids may be studied.

REACTIONS CAUSING DEPOSITION OF SOLIDS

Specimens of solid materials obtained from Shadman well 34 located in West Pakistan were subjected to optical, X-ray, and chemical tests. In 1964 solids were obtained from a mild-steel well screen that had been removed from the well and stored in air for less than a month before samples were obtained. The samples collected in 1964 were from three types of deposits: deposits filling the slots of the well screen; deposits on the outside of the well screen (on the aquifer side of the screen); and deposits on the inside wall of the well screen.

As shown in figures 2 and 3, the material found filling the slots was not homogeneous. The layers or zones were roughly symmetrical about central zone 3. Neither zones 2 nor 4 were in contact with the mild-steel screen, these zones being physically separated from the steel by zones 1 and 5. A summary of the phases found is presented in table 1. The pattern may have been influenced by catalytic effects of primary deposits.

The zones in contact with the steel (zones 1 and 5) are composed largely of silt-sized material with a few fine sand-sized grains which, upon optical examination, appear to be quartz and white mica. By X-ray diffrac-

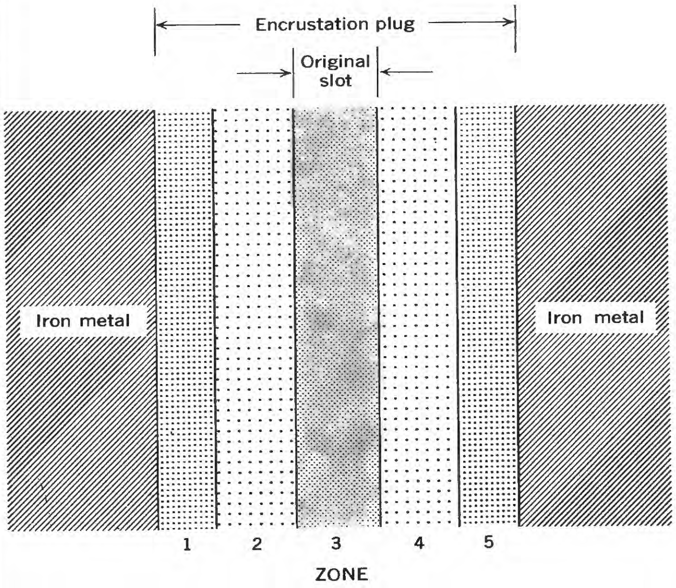

FIGURE 2.—Diagrammatic sketch, encrustation plug, corroded steel casing slot, Shadman well 34, West Pakistan.

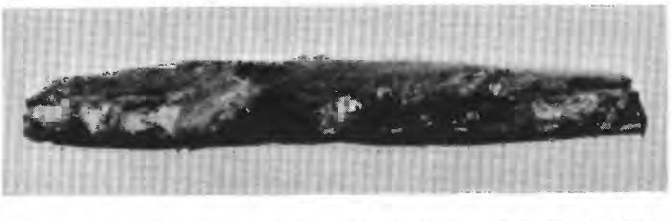

FIGURE 3.—Encrustation plug, steel casing slot, Shadman well 34, West Pakistan.

TABLE 1.—*Identifications of solid phases found in slot filling of the mild-steel well casing removed from Shadman well 34, West Pakistan*

Zone	*Phases identified*
1 and 5	Siderite, Mn_3O_4 (spinel), $Cu(OH)_2$, hausmannite, magnetite(?), maghemite(?), and detrital(?) quartz and white mica.
2 and 4	$Cu(OH)_2$, mackinawite, and detrital(?) quartz.
3	Calcite, siderite, mackinawite, detrital(?) quartz, mica, and plagioclase(?) feldspar.

tion zones 1 and 5 (in contact with the mild steel) were found to consist chiefly of approximately equal amounts of siderite ($FeCO_3$) and a mixture of very fine grained cubic Mn_3O_4 (spinel structure) and $Cu(OH)_2$. The largest siderite diffraction peaks are apparently displaced from the positions expected for siderite to smaller unit cell spacings. Possibly the apparent shift in the positions of the peaks may be due to the substitution of Mn^{+2} for Fe^{+2} in the siderite.

Two magnetic separation methods were applied to materials from zones 1 and 5 (the zones adjacent to the mild-steel surfaces), but both magnetic separates were apparently identical from X-ray diffraction studies. X-ray diffractograms of the two magnetic separates showed only siderite, even with strong pulse height discrimination. The two apparently identical magnetic separates were combined to make a single magnetic fraction and photographed using iron X-radiation. The results of the iron X-ray photography are tabulated in table 2. A study of the film exposed by iron radiation showed siderite as the dominant phase with presumably lesser amounts (lighter lines) of $Cu(OH)_2$ and both forms of Mn_3O_4. The strongest diffraction lines of both the isometric Mn_3O_4 (spinel structure) and the tetragonal Mn_3O_4 (hausmannite) were found. At least one iron oxide and possibly both magnetite (Fe_3O_4) and maghemite (Fe_2O_3) are present. A phase intermediate between magnetite and maghemite, such as the phase described by Harrison and Peterson (1965), also is a possibility.

Zones 2 and 4 lying between innermost zone 3 of the slot filling and zones 1 and 5 in contact with the mild steel also were examined. Zones 2 and 4 were composed of a dull, metallic gray material that was quite brittle. There was noticeable gradation between zones 1 and 2 and between zones 5 and 4. Both inner zones 2 and 4 were made of botryoidal masses coated with silt-sized quartz. Both the inner zones (2 and 4) had relatively more or perhaps more coarsely crystalline $Cu(OH)_2$ than the outer zones (1 and 5). Both the inner zones (2 and 4) contained mackinawite (tetragonal FeS) but no carbonate phase was detected.

Innermost zone 3, found in the middle of the filled slots, also was botryoidal in texture with silt-sized quartz. Upon crushing some of the botryoidal masses of the innermost zone, it was found that some contained black massive material, but others contained blood-red material with a boxwork structure. The material of the innermost zone was too fine grained to permit physical separation of the botyroidal masses for a comparative X-ray study. X-ray investigation of the bulk material of the innermost zone yielded rather poorly resolved diffractograms; therefore some identifications were questionable. The material was found to be mostly quartz and calcite with siderite and mackinawite. Minor amounts of a phase which gave a diffractogram peak at 10 A (angstroms) may have been mica. Apparently a feldspar was present also, possibly plagioclase, but a definite identification was not possible. This sequence suggests that catalytic surface effects as well as water composition may have influenced the nature of the deposit. Hem (1964) found such effects in his study of manganese. Localized corrosion processes also may have contributed to the structure by producing products not predictable on the basis of this type of analysis; these products, in turn, may have

TABLE 2.—*A comparison of the composition in weight percent by spectrographic analysis of materials found on the well screen of Shadman well 34, West Pakistan*

[Slot-filling zones shown in figure 2. Spectrographic analysis by Pauline Dunton. Materials separated by Roger Wolff and Pauline Dunton. Minerals identified by Blair Jones using X-ray diffraction methods. Nd, not determined; ...., no sample. Abundance of phases decreases toward bottom of lists]

	Slot filling									Crust from outside of screen			Crust from inside of screen		
	Zones 1 and 5, next to mild steel			Zones 2 and 4			Zones 3, innermost zone								
Element	Wolff	Dunton	Minerals	Wolff	Dunton	Minerals	Wolff	Dunton	Minerals	Wolff	Dunton	Minerals	Wolff	Dunton	Minerals
Fe	34	48	Siderite	....	44	$Cu(OH)_2$	16	27	Quartz	37	....	Siderite	32	....	$Cu(OH)_2$.
Ca	.1	Nd	Mn_3O_4 (spinel).	....	Nd	Mackinawite.	5	Nd	Calcite	.5	....	$Cu(OH)_2$ (?).	.1	....	Mackinawite.
Mn	.5	.5	$Cu(OH)_2$	....	.1	Quartz	.1	.1	Siderite	.5	....	Mn_3O_4 (spinel).	.1	....	Siderite.
Co	.03	.03	Hausmannite.	....	.007	....	.007	.003	Mackinawite.	.01	....	Calcite	.007	....	$Mn(OH)_2$ (?).
Cr	.05	.1	Magnetite (?).	....	.007	....	.003	.0007	Mica(?)	.07	....	....	.01	....	....
Cu	.7	1.0	Maghemite (?).	....	.05	....	.03	.05	Feldspar (?).	.5	....	....	.1	....	....
Ni	.3	.3	....	....	.03	....	.005	.005	....	.3	....	....	.03	....	....
S [1]	4	Nd	....	....	Nd	....	18	Nd	....	3	....	....	14	....	....

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[1] Analyses by Pauline Dunton using X-ray fluorescence.

catalyzed precipitation of compounds found in the deposit.

Material also was obtained from inside the well screen removed from Shadman well 34. This sample was flaky in appearance and consisted of massive metallic material coated by granular material on the side exposed to the water within the well screen. The granular material could not be separated from the massive metallic material owing to the fineness of grain and thinness of the granular coating. X-ray diffractometer study showed $Cu(OH)_2$ as the most abundant phase, with very small amounts of (or extremely fine-grained) mackinawite, siderite, and possibly $Mn(OH)_2$.

The phases identified in the study of materials collected in 1964 from the screen of Shadman well 34 are summarized in table 1, together with available chemical data from the same well. Comparisons of the reported compositions of samples prepared by Roger Wolff and Pauline Dunton show that the analytical data are not absolute in nature, but show relative abundances of the several elements reported in the samples. The chemical analyses do not accurately reflect the relative proportions of the solids as determined by X-ray diffraction. The various grain sizes mentioned in the descriptions of the samples would lead one to expect the poor agreement shown in table 2. The presence of quartz (Si not determined) and amorphous materials such as $Fe(OH)_3$ also would complicate relation of chemical composition to apparent relative amounts of materials found by X-ray study. The chemical data do provide a test for the X-ray data, however, in that all the phase identifications appear to be reasonable. All samples in which Cu-bearing phases were found by X-ray study did have appreciable Cu as shown by chemical analysis. All the samples in which Mn-containing phases were found by X-ray study did contain Mn as shown by chemical analysis. No further interpretation of the data in table 2 seems warranted.

In addition to the materials described thus far, all of which were collected in 1964, a sample was scraped off the inside of a pump column installed in Shadman well 34 before the 1965 field season. Both the well screen sampled in 1964 and the pump column sampled in 1965 were of mild steel. However, the well screen had been stored in air prior to sampling, whereas the pump column sample was collected in 1965 immediately after removing it from the well. An X-ray study of the pump column sample showed magnetite apparently to be the most abundant phase, with quartz and a small amount of another phase giving a diffraction peak at 10 A (possibly a mica). A surface film of the same sample exposed by iron X-radiation revealed evidence of the metastable polymorphs of Fe_3S_4, smythite (rhombohedral) and greigite (cubic). A systematic study of the film showed that mackinawite; pyrrhotite, $Fe_{1-x}S$; valeriite, $Cu_2Fe_4S_7$(?); pyrite, FeS_2; copper hydroxide, $Cu(OH)_2$; manganese hydroxide, $Mn(OH)_2$; manganese spinel, Mn_3O_4 (isometric); and hausmannite, Mn_3O_4 (tetragonal), were not detectable by the X-ray technique used, if indeed they were present at all.

The results of the mineralogic study of the solids found upon the mild-steel well screen, well casing, and pump column of Shadman well 34 give tentative identifications of possible occurring phases. Presumably the phases identified have been deposited from the water flowing through or standing in, or immediately outside of, the well casing and screen. Even if the existence of each suggested phase is accepted, there is no way of telling whether the phases found are primary precipitates formed directly in place by precipitation from a true solution, or whether suspended particulate matter had deposited as a sludge of encrustant on the various surfaces. Possibly the iron-bearing phases identified are related to corrosion of the well casing and would not have been formed on an iron-free substrate in contact with the same water. Catalytic effects of primary precipitates on further precipitation already have been mentioned as a possibility. There also is the possibility that certain precipitating solids were swept away, and thus not detected.

In spite of the uncertainty of the origins of the solids tentatively identified, they must be considered in any reasonably complete study of corrosion and encrusting properties of the water. The data for composition of water samples were analyzed to determine the states of reaction (supersaturation, equilibrium, and unsaturation) with respect to most of the oxides, hydroxides, carbonates, sulfides, and sulfates of the metal cations other than the alkali metal cations. The reactions used are summarized in the section on "Data analysis." Extreme values of the $\Delta\mu_R$ and CR are given in table 3, along with the identification of the wells yielding the extreme values. Shadman well 34, the well from which the solids were obtained for detailed examination, is not listed in table 3. Water of Shadman well 34 is not as far from equilibrium as some of the others sampled in spite of the rich suite of exotic phases identified such as $Mn(OH)_2$ and $Cu(OH)_2$.

Both positive and negative values of $\Delta\mu_R$ are given for supersaturation. The reason is that the redox reactions were all written to yield electrons on the right-hand side of the equation. Sometimes the solid appears on the left side of the reaction (reactant) and sometimes on the right side of the reaction (product). For supersaturated states, the sign $\Delta\mu_R$ will be + if the solid is on the left side of the reaction and − if the solid

TABLE 3.—*Ranges of numerical results of data analysis for possible reactions of waters and solids*

[Reaction numbers are the same as in text and appendixes; Ss, supersaturated; Un, unsaturated]

Reaction	Mineral name	Composition	Maximum values of $\Delta\mu_R$ and CR, well water in which found, state of reaction				Minimum values of $\Delta\mu_R$ and CR, well water in which found, state of reaction			
			Well identification	State of reaction	$\Delta\mu_R$ (kcal)	CR	Well identification	State of reaction	$\Delta\mu_R$ (kcal)	CR
0	Cuprite	Cu_2O	Zaparwal 1[1]	Ss	8.43	1.04×10^{3}	Sangla Hill 2[1]	Un	−4.09	3.06×10^{-2}
1	Tenorite	CuO	Sangla Hill 2[1]	Ss	3.25	2.54×10^{2}	Kauwa[2]	Un	−7.11	9.09×10^{-6}
2		$Cu(OH)_2$	do	Ss	1.48	1.25×10^{1}	do	Un	−8.98	4.27×10^{-7}
3	Azurite	$Cu_3(CO_3)_2(OH)_2$	do	Ss	9.75	2.46×10^{2}	do	Un	−25.3	5.30×10^{-5}
4	Malachite	$Cu_2(CO_3)(OH)_2$	do	Ss	7.56	6.32×10^{2}	do	Un	−16.1	6.54×10^{-5}
5	Covellite	CuS	Mona 113[1]	Ss	26.2	2.15×10^{19}	Nasser 3[3]	Ss	20.5	2.65×10^{14}
6	Chalcocite	Cu_2S	Mona 83[1]	Ss	36.7	2.22×10^{13}	Sangla Hill 2[1]	Ss	22.8	2.87×10^{8}
7	Rhodochrosite	$MnCO_3$	Dalori[2]	Ss	.632	2.85×10^{0}	Rashda[3]	Un	−1.94	4.18×10^{-2}
8		$Fe(OH)_2$	do	Un	−3.36	3.82×10^{-3}	Mut[3]	Un	−6.12	4.38×10^{-5}
9	Siderite	$FeCO_3$	do	Ss	1.60	1.42×10^{1}	Rashda[3]	Un	−.47	4.61×10^{-1}
10	Magnesite	$MgCO_3$	Lyallpur 54[1]	Ss	.53	2.44×10^{0}	Mut[3]	Un	−3.49	3.30×10^{-3}
11	Dolomite	$CaMg(CO_3)_2$	Mona 83[1]	Ss	2.06	3.18×10^{1}	Rashda[3]	Un	−5.48	1.25×10^{-4}
12	Calcite	$CaCO_3$	do	Ss	.83	4.03×10^{0}	do	Un	−2.68	1.23×10^{-2}
13	Mackinawite[4]	FeS								
14	Chalcopyrite[4]	$CuFeS_2$								
15	Bornite[4]	Cu_5FeS_4								
16		$Mn(OH)_2$	Shahkot 251[1]	Un	−6.92	7.25×10^{-6}	Rashda[3]	Un	−10.3	4.69×10^{-8}
17	Anhydrite	$CaSO_4$	Khaipur K12[1]	Un	−.221	6.82×10^{-1}	Kharga 1A[3]	Un	−4.98	3.18×10^{-4}
18	Gypsum	$CaSO_4\cdot2H_2O$	do	Un	−.0147	9.76×10^{-1}	do	Un	−4.89	3.66×10^{-4}
0	Iron	Fe	Dalori[2]	Un	−13.6	1.75×10^{-10}	Sangla Hill 2[1]	Un	−48.6	1.09×10^{-36}
1	Magnetite	Fe_3O_4	do	Ss	−7.20	5.30×10^{1}	do	Ss	−37.3	1.59×10^{9}
2	Ferric hydroxide or "limonite"	$Fe(OH)_3$	do	Un	5.62	9.19×10^{-5}	Mona 113[1]	Ss	−5.00	3.32×10^{7}
3		$H_2S\text{-}SO_4^{-2}$	Nasser 1[3]		−31.64		Sangla Hill 2[1]		−129	
4	Pyrolusite	MnO_2	Dalori[2]	Un	35.0	7.2×10^{-26}	do	Un	1.11	1.49×10^{-1}
5	Hausmannite	Mn_3O_4	Gamarshin[3]	Un	35.2	4.80×10^{-9}	do	Un	.96	5.79×10^{-1}
6	Bixbyite	Mn_2O_3	Dalori[2]	Un	31.3	5.76×10^{-12}	do	Ss	−2.72	1.01×10^{1}
7	Pyrite (H_2S reaction)	FeS_2	Nasser 3[3]	Ss	−24.0	7.84×10^{16}	do	Ss	−44.2	5.41×10^{32}
8	Copper	Cu	Dalori[2]	Ss	9.48	6.54×10^{6}	do	Un	−12.3	7.92×10^{-10}
9	Hematite	Fe_2O_3	do	Ss	−4.09	2.94×10^{1}	do	Ss	−35.4	1.28×10^{13}
10	Pyrite (SO_4 reaction)	FeS_2	do	Ss	26.2	6.21×10^{18}	do	Un	−214	3.21×10^{-159}
[5] 11										
[5] 12										
13		$Mn(OH)_3$	Gamarshin 1[3]	Un	28.2	9.58×10^{-21}	Sangla Hill 2[1]	Un	7.86	1.52×10^{-6}

[1] West Pakistan.
[2] Nigeria.
[3] Egypt.
[4] No $G°$ data available.
[5] Used for distributing copper species.

NOTE.—See "Appendix 2" for detailed chemical data of wells listed.

is on the right. The state of the reaction is given to make the meaning of the $\Delta\mu_R$ values unequivocal.

Several regularities of behavior may be found in the data presented in table 3. The simple carbonates, such as $FeCO_3$ and $CaCO_3$, are relatively well behaved in that the maximum departures from equilibrium on the supersaturated side of equilibrium are only 1.6 and 0.83 kcal for siderite and calcite, respectively, and both have been found as solid phases. In terms of compositions of the solutions, maximum supersaturation (CR) is only 14. and 4.0, respectively. The inference drawn is that both phases may precipitate so rapidly that the solubilities of siderite and calcite are effective controls on the compositions of the ground waters in comparison to the apparent extreme departures from equilibrium of the other phases studied. Departure from equilibrium on the unsaturated side of equilibrium (−0.47 kcal for siderite and −2.68 kcal for calcite) may only indicate the lack of contact of the solid phases with the water, a condition due either to the complete absence of the carbonates from the aquifer(s) or at least to the absence of the carbonates along the flow paths of the waters withdrawn.

The simple oxides and hydroxides, including those of copper, iron, and manganese, apparently do not generally operate as effectively as the simple carbonates in controlling ground-water compositions. $CU(OH)_2$, a notable exception, has only 1.48 kcal as a maximum chemical potential for reaction, a value representing supersaturation of only a factor (CR) of 12.5. The anhydrous copper oxides, cuprite and tenorite, and the anhydrous iron oxides, magnetite and hematite, apparently react slowly enough so that very large departures from equilibrium may occur, as shown in table 3.

The largest observed departures from equilibrium involve sulfides. The departures from equilibrium range from at least +20 kcal on the positive side to as large a negative potential as −214 kcal. Although the reactions are probably very complicated in detail, the general inference may be drawn that sulfides do not react readily.

Table 4, drawn from table 3, summarizes the phases with which the aqueous solutions studied were found to be consistently supersaturated. Although the data are fragmentary and inconclusive, several tentative inferences may be drawn. The simple oxides listed apparently do not precipitate rapidly, as the departures from equilibrium (apparent supersaturations) range from −2.72 kcal to −35.4 kcal. In contrast, the simple carbonates ($CaCO_3$, $FeCO_3$, $MnCO_3$) depart from equilibrium by only 0.63 to 1.60 kcal as maximum supersaturations. As the carbonates become more complex and hydrated, supersaturated solutions appar-

TABLE 4.—*$\Delta\mu_R$ for waters supersaturated with respect to solids that might precipitate from the well water as sampled at the wellhead*

[All values are in kilocalories]

	$\Delta\mu_R$ (max)	$\Delta\mu_R$ (min)
Cu_2O	8.43	
CuO	3.25	
Mn_2O_3		−2.72
Fe_2O_3	−4.09	−35.4
$CaCO_3$	.83	
$FeCO_3$	1.60	
$MnCO_3$	.63	
$CaMg(CO_3)_2$	2.06	
$Cu_2CO_3(OH)_2$	7.56	
$Cu_3(CO_3)_2(OH)_2$	9.75	
$Cu(OH)_2$	1.48	
$Fe(OH)_3$		−5.00
Cu	9.48	
CuS	26.2	20.5
Cu_2S	36.7	22.8
FeS_2 (H_2S reaction)	−24.0	−44.2
FeS_2 (SO_4 reaction)	26.2	
Fe_3O_4	−7.2	−37.3

ently deviate by as much as 9.75 kcal from equilibrium. The only carbonates found to precipitate are $FeCO_3$ and $CaCO_3$.

The simple sulfides considered here are quite different from the other solids. Although examined only in terms of reactions involving precipitation from aqueous phases containing sulfide (except for pyrite, in which both sulfide and sulfate reactions were considered), the sulfides studied departed from equilibrium with the coexisting aqueous phase markedly more than did the complex carbonates, the simple carbonates, and the oxides.

From the work of Barnes, Stuart, and Fisher (1964) it may be concluded that apparently pyrite dissolved into some aqueous solutions (including mine water containing H_2S, at pH of 5.4 or less) rapidly enough to come to saturation. Such is not the case in the sulfide-containing solutions at higher pH's as reported on here. Not only do sulfides not precipitate readily from sulfide-containing solutions but apparently the presence of sulfide species at pH values of 7.0 or more may inhibit the solution of the sulfide-containing phases if they be present.

TABLE 5.—*States of reaction including all well waters and summary of phases found in samples from Shadman well 34, West Pakistan*

Solid name	Super-saturated for all waters tested	Unsaturated for all waters tested	Both super-saturation and unsaturation found	Phase was found in mineral analysis
Cu_2O, cuprite			Yes	No.
CuO, tenorite			Yes	No.
$Cu(OH)_2$, copper hydroxide			Yes	Yes(?).
$Cu_3(CO_3)_2(OH)_2$, azurite			Yes	No.
$Cu_2(CO_3)(OH)_2$, malachite			Yes	No.
CuS, covellite	Yes			No.
Cu_2S, chalcocite	Yes			No.
$MnCO_3$, rhodochrosite			Yes	No.
$Fe(OH)_2$, ferrous hydroxide		Yes		No.
$FeCO_3$, siderite			Yes	Yes.
$MgCO_3$, magnesite			Yes	No.
$CaMg(CO_3)_2$, dolomite			Yes	No.
$CaCO_3$, calcite			Yes	Yes.
$Mn(OH)_2$, manganous hydroxide.		Yes		Yes(?).
$CaSO_4$ anhydrite		Yes		No.
$CaSO_4 \cdot 2H_2O$, gypsum		Yes		No.
Fe, iron metal		Yes		Yes (well casing).
Fe_3O_4, magnetite	Yes			Yes.
$Fe(OH)_3$, ferric hydroxide			Yes	Yes.
MnO_2, pyrolusite		Yes		No.
Mn_3O_4, hausmannite		Yes		Yes(?).
Mn_2O_3, bixbyite			Yes	No.
FeS_2, pyrite (H_2S reaction)	Yes			No.
Cu, copper metal			Yes	No.
Fe_2O_3, hematite	Yes			No.
FeS_2, pyrite(SO_4 reaction)			Yes	No.
$Mn(OH)_3$, manganic hydroxide.		Yes		No.

The small amount of data on the apparent behavior of the solid phases is summarized in table 5, which gives the nature of the departures from equilibrium of the solids presented in table 3. Also presented in table 5 is the list of solids which were found on substrates in Shadman well 34. It is unfortunate that samples of encrustants were not available from wells other than Shadman well 34. Because the water from Shadman well 34 does not represent the extreme value for the departure from equilibrium for any solid, it would be expected that more solids than those listed may be forming on substrates on other wells. In any event, Shadman well 34 water, although it is supersaturated with several solids, is only precipitating one stable phase, calcite. Siderite, ferric hydroxide, and magnetite are metastable relative to (more soluble than) hematite. $Cu(OH)_2$ is metastable relative to (more soluble than) any other copper phase considered.

Table 6 gives the detailed chemistry of Shadman well 34. Not only is $Cu(OH)_2$ metastable with respect to the other copper-bearing phases, but the bulk discharge of the well is unsaturated with $Cu(OH)_2$. The water obtained from Shadman well 34 is unsaturated with both hausmannite (tentatively identified) and $Mn(OH)_2$.

TABLE 6.—*Results of chemical analysis and data analysis, Shadman well 34, West Pakistan*

[Extracted from computer program (see "Appendix 2"). Field *Eh*, pH, Fe^{+2}, HCO_3, by F. E. Clarke, USAID, and West Pakistani scientists, March 1965; other chemical data by laboratories of the U.S. Geological Survey, May 1965]

A. Intrinsic thermodynamic properties of water—general characteristics

pH	Oxidation-reduction potential (volt)	Temperature (°C)	Ionic strength	Partial pressure, CO_2 (atmosphere)	Aqueous CO_2 (molality)	Aqueous CO_2 (ppm)	Standard potential Fe_3S_4	Log activity of SO_4^{-2} at equilibrium with H_2S	Log activity of iron in equilibrium with pyrite at measured SO_4^{-2}
7.49	0.0870	28.00	0.01089	0.0116517	0.000368	16.19	0.739	40.4757	61.4646

B. Intrinsic thermodynamic properties of water—ionic data

	Ion	Concentration (ppm)	Activity coefficient	Molality	Activity molal scale
0	CA	62. 000	0. 665516	1. 5469@−03	1. 0295@−03
1	MG	27. 000	. 680260	1. 1106@−03	7. 5547@−04
2	NA	61. 000	. 897684	2. 6534@−03	2. 3819@−03
3	K	3. 100	. 894677	7. 9280@−05	7. 0930@−05
4	CL	23. 000	. 894677	6. 4875@−04	5. 8042@−04
5	SO4	45. 000	. 649373	4. 6845@−04	3. 0420@−04
6	HCO3	356. 680	. 897684	5. 8456@−03	5. 2475@−03
7	FE 2	. 400	. 665516	7. 1624@−06	4. 7667@−06
8	FE 3	. 000	. 429915	. 0000@+00	. 0000@+00
9	MN 2	. 117	. 665516	2. 1272@−06	1. 4157@−06
10	CU 1	. 036	. 894677	5. 7035@−07	5. 1028@−07
11	CU 2	. 004	. 665516	5. 9737@−08	3. 9756@−08
12	HS	. 388	. 896202	1. 1743@−05	1. 0524@−05
13	H2S	. 100	1. 000000	2. 9285@−06	2. 9285@−06
14	CU2OH2	. 000	. 693776	4. 9218@−11	3. 4146@−11
15	CUTOT	. 040			
16	H2STOT	. 500			

C. Thermodynamic state of water with respect to coexisting solid phases undergoing hydrolysis reactions

	Solid phase	Activity product	Equilibrium constant at observed temperature	Activity product/ equilibrium constant	Cation, actual/ cation, equilibrium	Cation at equilibrium (molality)	Cation at equilibrium (ppm)	Actual chemical potential (k cal)
0	CU2O	2. 4866@+02	1. 9691@−02	1. 2628@+04	1. 1238@+02	6. 8230@−09	4. 3353@−04	5. 65170
1	CUO	3. 7967@+07	5. 9293@+07	6. 4033@−01	6. 4033@−01	9. 3291@−08	5. 9277@−03	−. 26678
2	CU(OH2	3. 7967@+07	1. 2311@+09	3. 0839@−02	3. 0839@−02	1. 9371@−06	1. 2308@−01	−2. 08204
3	AZURIT	3. 8920@−18	1. 0836@−18	3. 5916@+00	1. 5314@+00	3. 9007@−08	2. 4785@−03	. 76519
4	MALACH	1. 2156@−05	1. 6113@−06	7. 5441@+00	2. 7467@+00	2. 1749@−08	1. 3819@−03	1. 20935
5	CUS	1. 1118@+02	9. 1162@−16	1. 2196@+17	1. 2196@+17	4. 8979@−25	3. 1122@−20	23. 54499
6	CU2S	7. 2821@−04	2. 2282@−28	3. 2682@+24	1. 8078@+12	3. 1549@−19	2. 0046@−14	33. 78096
7	MNCO3	1. 1401@−11	1. 4281@−11	7. 9836@−01	7. 9836@−01	2. 6644@−06	1. 4638@−01	−. 13477
8	FE(OH2	4. 5522@+09	1. 3113@+13	3. 4715@−04	3. 4715@−04	2. 0632@−02	1. 1522@+03	−4. 76720
9	FECO3	3. 8389@−11	2. 0247@−11	1. 8960@+00	1. 8960@+00	3. 7777@−06	2. 1097@−01	. 38286
10	MGCO3	6. 0842@−09	1. 1100@−08	5. 4810@−01	5. 4810@−01	2. 0262@−03	4. 9261@+01	−. 35985
11	DOLOMI	5. 0444@−17	1. 0000@−17	5. 0444@+00	5. 0444@+00	3. 0666@−04	1. 2291@+01	. 96848
12	CACO3	8. 2910@−09	4. 2276@−09	1. 9612@+00	1. 9612@+00	7. 8876@−04	3. 1614@+01	. 40309
13	FES	1. 3331@+04	---------	---------	---------	---------	---------	---------
14	CUFES2	1. 4822@+06	---------	---------	---------	---------	---------	---------
15	BORNIT	7. 8599@−01	---------	---------	---------	---------	---------	---------
16	MN(OH2	1. 3520@+09	1. 3859@+15	9. 7548@−07	9. 7548@−07	2. 1807@+00	1. 1980@+05	−8. 28292
17	ANHYDR	3. 1317@−07	3. 4675@—05	9. 0315@−03	9. 0315@−03	1. 7128@−01	6. 8649@+03	−2. 81698
18	GYPSUM	3. 1317@−07	2. 4319@−05	1. 2877@−02	1. 2877@−02	1. 2013@−01	4. 8146@+03	−2. 60467

D. Thermodynamic state of water with respect to coexisting solid phases undergoing oxidation-reduction reactions

	Solid phase	Standard state potential at observed temperature (volts)	Calculated oxidation-reduction potential at observed temperature (volts)	Cation, actual/ cation, equilibrium	Cation at equilibrium (molality)	Cation at equilibrium (ppm)	Actual chemical potential (kcal)
0	FE MET	−0. 4398	−0. 5989	1. 1097@−23	6. 4541@+17	3. 6044@+22	−31. 631911
1	FE304	. 9763	−. 3370	5. 3715@+04	1. 3334@−10	7. 4467@−06	−19. 554358
2	FE(OH3	1. 0548	. 0301	8. 9623@+00	7. 9917@−07	4. 4631@−02	−1. 312443
3	H2S	. 3028	−. 2416	1. 0174@−44	. 0000@+00	. 0000@+00	−60. 622113
4	MN02	1. 2270	. 5066	9. 0480@−15	2. 3510@+08	1. 2916@+13	19. 352011
5	MN304	1. 8166	. 5505	6. 7375@−06	3. 1572@−01	1. 7345@+04	21. 379154
6	MN203	1. 4406	. 4474	9. 3150@−07	2. 2836@+00	1. 2546@+05	16. 621050
7	PY H2S	−. 1409	−. 5464	1. 5798@+21	4. 5338@−27	2. 5320@−22	−29. 211877
8	CU MET	. 3370	. 1159	9. 2846@+00	6. 4340@−09	4. 0882@−04	1. 333586
9	FE203	. 7242	−. 3005	3. 0548@+06	2. 3447@−12	1. 3094@−07	−17. 872735
10	PY SO4	. 3662	−. 1981	. 0000@+00	. 0000@+00	. 0000@+00	−92. 032368
11	CUDIST	---------	---------	---------	---------	---------	---------
12	CUDIST	---------	---------	---------	---------	---------	---------
13	MN(OH3	1. 9242	. 9310	7. 5138@−15	2. 8310@+08	1. 5553@+13	19. 463210

Two alternative interpretations are obvious if the data are correct. Either some of the solids are indeed much less soluble than data in the literature indicate, or there are local conditions within the aquifer-well system which are not represented by the water discharged from the well. The second alternative is much more likely. The appearance of the well screen as shown in figure 4 is not uniform. Heavily encrusted and bare metal areas are apparent. Because detailed knowledge of the local properties of the water in the aquifer and in the intake areas is lacking, more specific interpretation of the data at hand does not seem warranted.

The chemical data do give the bulk properties of the water from the well, and it is the mixture of incompatible waters that gives rise to the troublesome encrustations such as were described from Shadman well 34. Detailed information on microenvironmental conditions within the intake (screen) and aquifer should be sought to aid in reaching an understanding of local corrosion attack or fouling of well screens and other parts of the well installation. This will require remote sensing equipment not yet perfected. The bulk properties of the water discharging from the well are equally important, since they shed light on corrosion problems above the intake, and possibly on the screen. As stated earlier, a test of the applicability of the chemical data analysis to corrosion problems may be illustrated by the comparison of predictions based upon the chemical characteristics of the water with the observed corrosive properties. Regardless of the uncertainties, any high order correlations between bulk water properties and corrosion and encrustation behavior are useful.

Corrosion test probes were introduced into nine wells. Mild (plain carbon) steel, the material most often used in the well construction, was one of the materials tested in the nine wells. Curves showing the corrosion probe results of nine wells (Dalori and Ngala, Nigeria; Kharga 1, Nasser 1, and Nasser 3, Egypt; and Shadman 27, Shadman 47, Shahkot 251, and Shahkot 252, West Pakistan) are given in figures 5 through 13. The corrosion effect (metal penetration or metal loss), as indi-

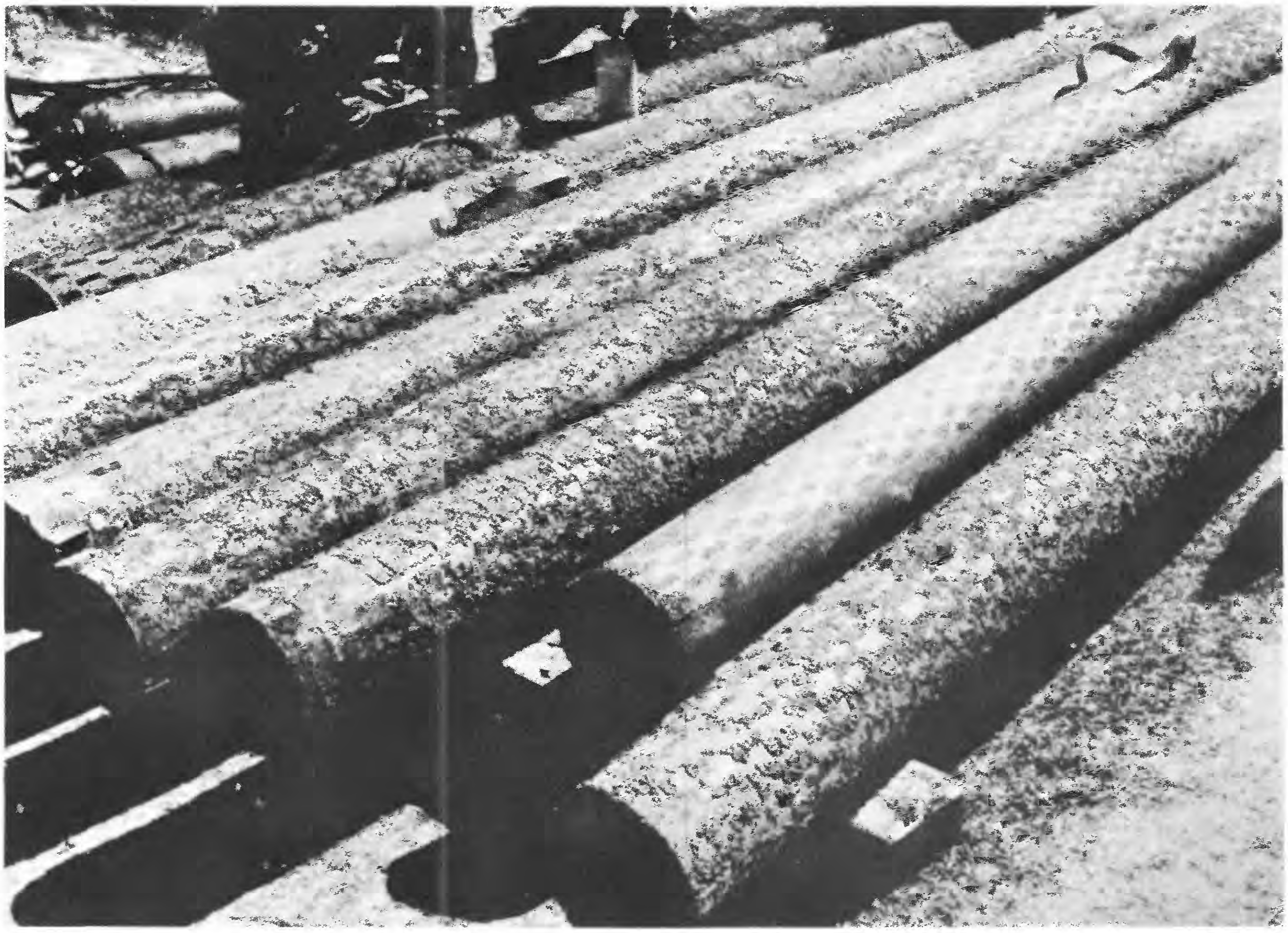

FIGURE 4.—Encrusted slotted casing, Shadman well 34, West Pakistan.

cated by the varying slopes in the corrosion curves in the plots for some of the wells, is not a simple function of time. In these cases it is not known whether there were intermittent periods of more severe attack because of variations in water quality, intermittent formation and loss of protective film, or periodic occurrence of localized effects, such as concentration cell corrosion. Sampling of a localized corrosion phenomenon, such as pitting corrosion, by the relatively small and specifically located corrosion probe element is likely to be misleading without other evidence of metal damage.

Whatever the source of changes in corrosion rates, average corrosion represents the accumulated effects to whatever extent the probes represent the actual well. Because of the stated uncertainties, the solubilities

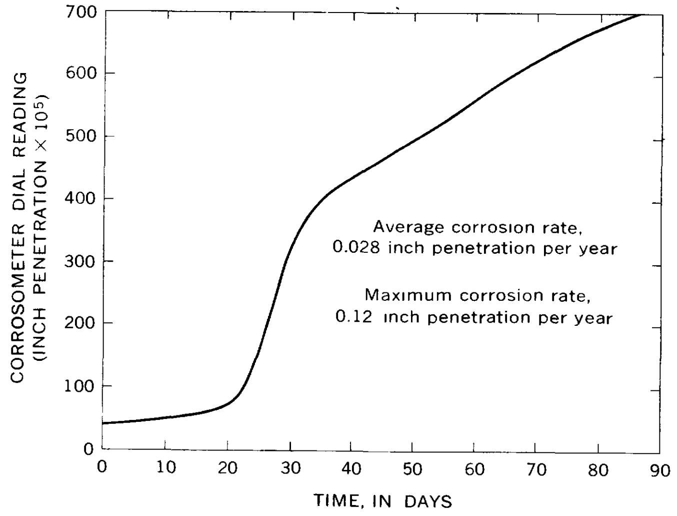

Figure 5.—Corrosion curve, mild steel, Dalori well, Nigeria.

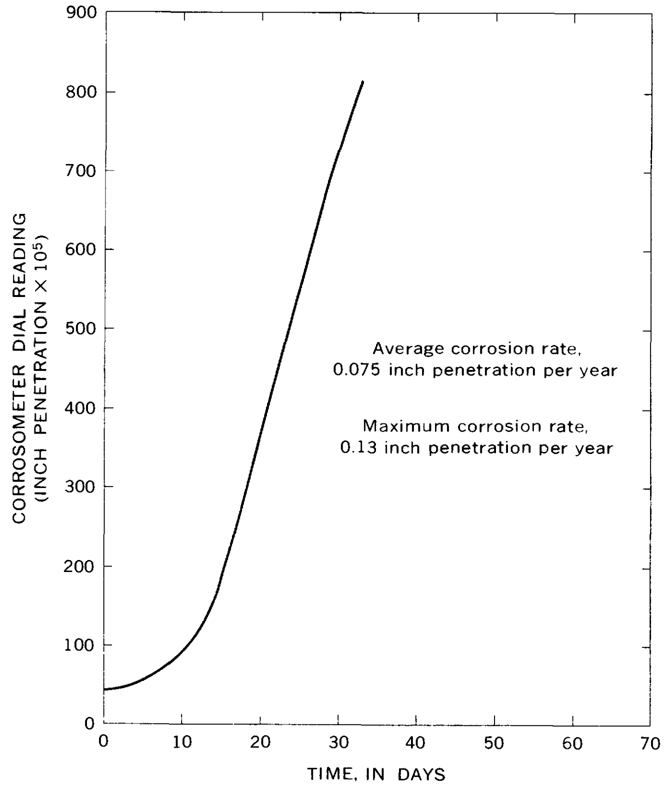

Figure 6.—Corrosion curve, mild steel, Ngala well, Nigeria.

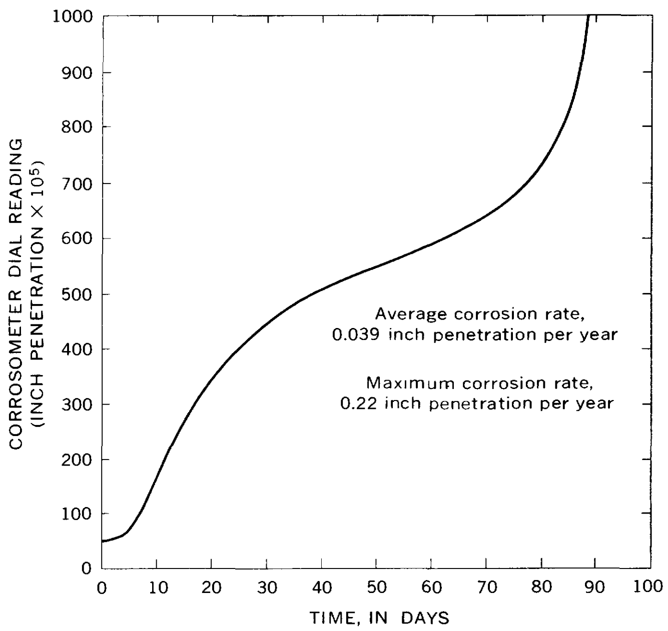

Figure 7.—Corrosion curve, mild steel, Kharga well 1, Egypt.

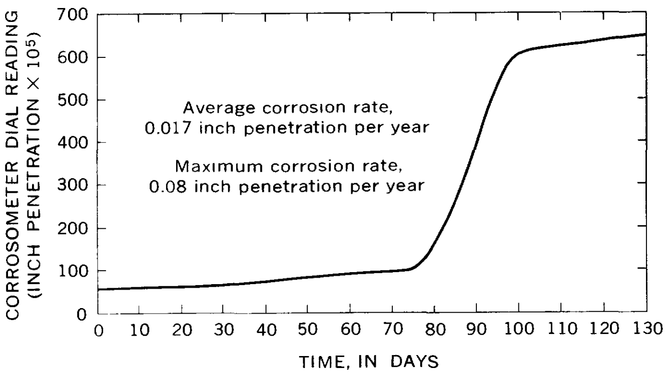

Figure 8.—Corrosion curve, mild steel, Nasser well 1, Egypt.

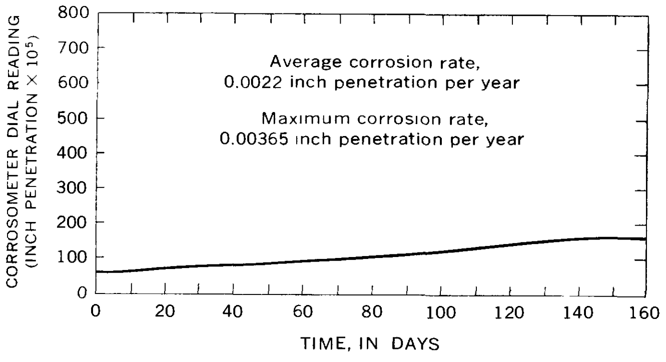

Figure 9.—Corrosion curve, mild steel, Nasser well 3, Egypt.

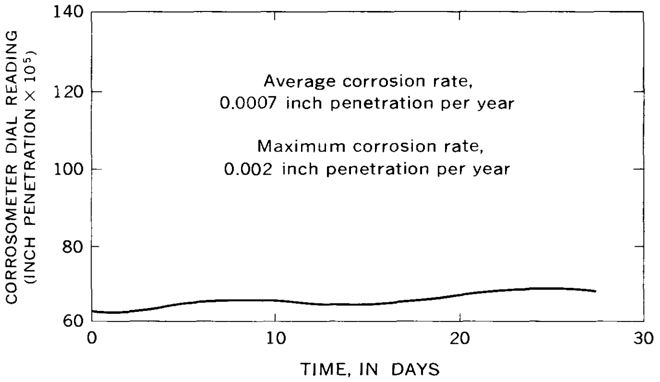

FIGURE 10.—Corrosion curve, mild steel, Shadman well 27, West Pakistan.

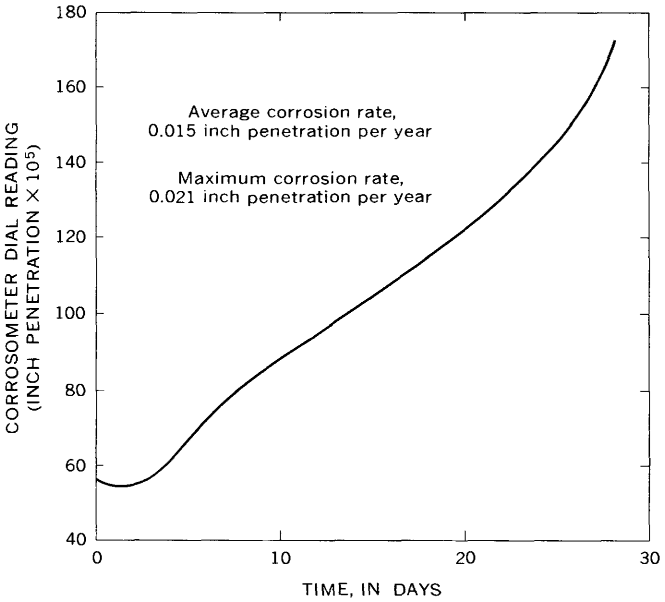

FIGURE 11.—Corrosion curve, mild steel, Shadman well 47, West Pakistan.

of possible reaction products are compared with both average corrosion rates and maximum corrosion rates as determined from the corrosion curves. Table 7 shows these comparisons in terms of $\log_{10}$ CR.

TABLE 7.—*Possible behaviors of solid phases capable of protecting iron from corrosion*

Value of $\log_{10}$ CR	State of reaction	Result
>0	Supersaturation	Protection; encrustation; catalytic coprecipitation.
$=0$	Equilibrium	Uncertain.
<0	Unsaturation	No protection; corrosion.

CORROSION AND ENCRUSTATION OF WELLS

The well waters examined are all unsaturated with respect to iron metal as shown in table 3. As a consequence, there is a potential to dissolve iron metal (corrode) into all the well waters reported here. Iron metal is the most soluble phase considered; every other iron-bearing phase tested in the data analysis is less soluble than iron metal. Not only is there a potential to dissolve iron metal, there is also the possibility of precipitation of the iron dissolved from the metal in other iron-bearing phases (corrosion products). Whether or not some of the iron-bearing phases found precipitating are in whole or in part corrosion products is moot because for all iron-bearing phases identified in Shadman well 34, potentials have been found to cause precipitation from the bulk waters studied even if corrosion of iron parts were not involved. There is a possibility for corrosive attack on iron by all the waters studied and there is evidence of it in the damage observed on corrosion probes and well parts. Consideration also needs to be given to the possibility of protective action by some of the solids, including corrosion products, which precipitate from the waters.

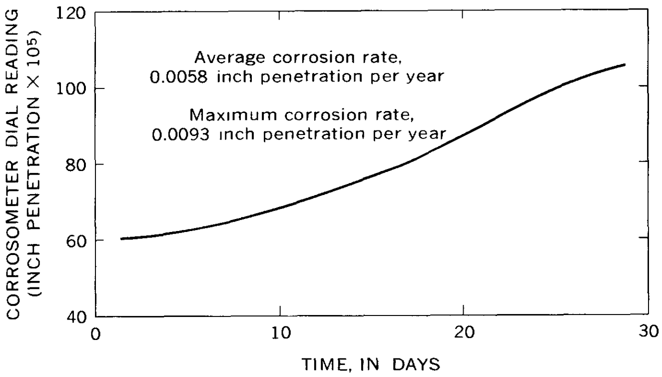

FIGURE 12.—Corrosion curve, mild steel, Shahkot well 251, West Pakistan.

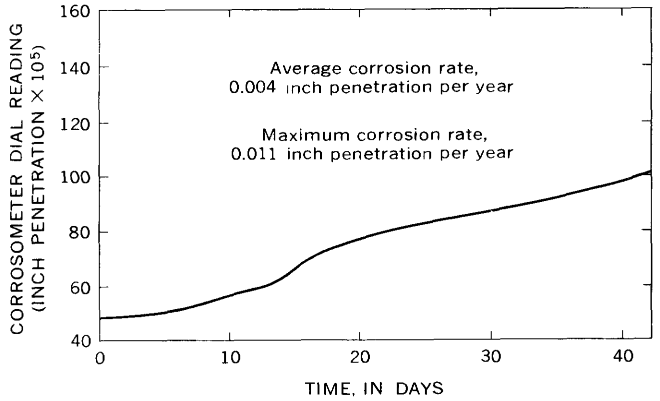

FIGURE 13.—Corrosion curve, mild steel, Shahkot well 252, West Pakistan.

The comparison of reaction states of possibly protective solid phases and the average corrosion rates of mild steel are given in figures 14 through 20. For only two of the solids tested, $CaCO_3$ (calcite) and $Fe(OH)_3$ (limonite), was a consistent relation found between the state of the reaction and corrosion rate (figs. 15, 16, 21, and 22). All solutions found supersaturated with one

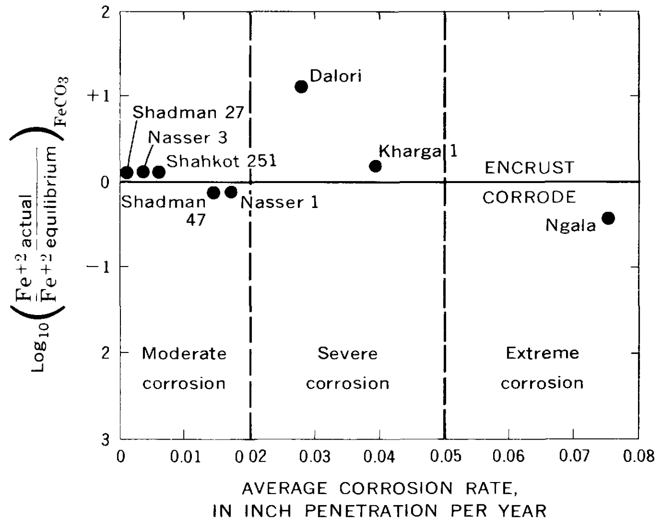

FIGURE 14.—Average corrosion rates plotted against reaction states, $FeCO_3$.

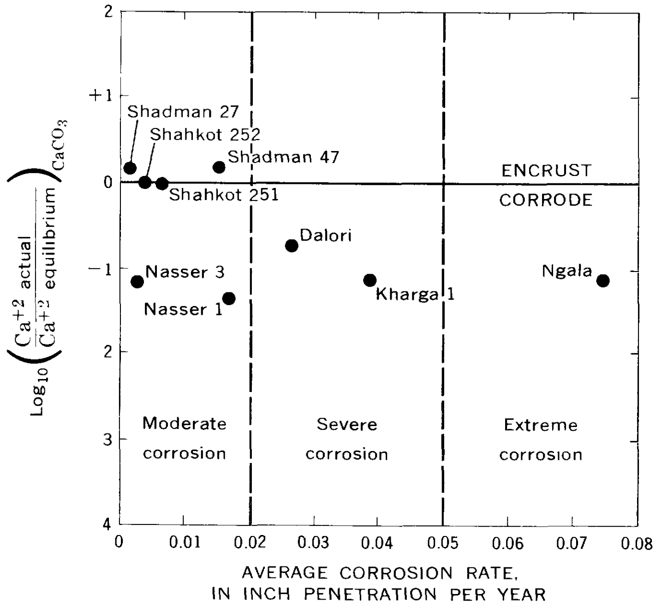

FIGURE 15.—Average corrosion rates plotted against reaction states, $CaCO_3$.

were also supersaturated with the other. There is no way of telling from present results, therefore, which of the two is effective in reducing corrosion rates, or whether both $Fe(OH)_3$ and $CaCO_3$ are effective. Certainly the long and rather successful role of $CaCO_3$ in reducing corrosion in water systems (see Langlier, 1946) indicates that $CaCO_3$ at slight supersaturation is likely to be a corrosion inhibitor in the wells studied. The role of $Fe(OH)_3$ is not known, but its ubiquitous occurrence in tubercular corrosion indicates $Fe(OH)_3$ is not an effective corrosion inhibitor. All the other phases considered (figs. 14, and 17 through 20), including $FeCO_3$, Fe_3O_4, iron metal, Mn_3O_4, and $Cu(OH)_2$ seem to give little, if any, corrosion protection to mild steel No regular relation is found in the plots made.

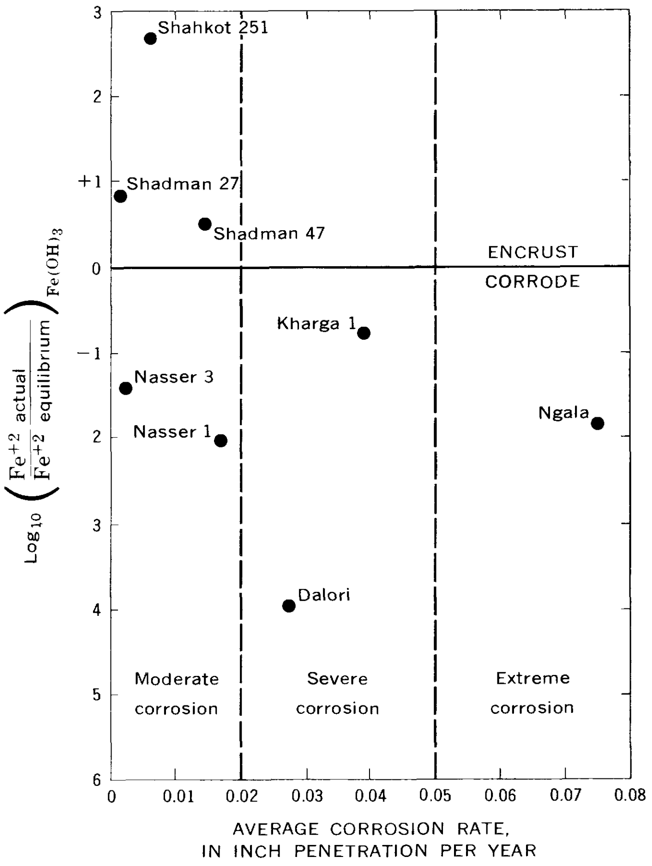

FIGURE 16.—Average corrosion rates plotted against reaction states, $Fe(OH)_3$.

The reaction states of the solids are compared with maximum corrosion rates in figures 21 through 27. No adjustment is made for the fact that equivalent corrosion damage may result from the general metal loss over a period of time as compared with intermittent severe attack during recurring periods of relatively short duration; nor does the analysis consider the well-established fact that severe localized attack may be more damaging than general corrosion because of extreme effects on susceptible parts. Neglecting these factors, exactly the same inferences may be drawn whether average or maximum corrosion rates are considered. $CaCO_3$ and $Fe(OH)_3$ (figs. 21 and 22) are the only phases that have consistent behavior. All the other solids (figs. 23 through 27) apparently are ineffective in giving protection against corrosion attack.

Such limitations as inability to collect reaction products immediately at the point of their formation; uncertainty about pertinent products lost from the metal surfaces with the flowing water; possible surface catalytic effects; deposition of reaction products that would not be predicted on the basis of water chemistry; and collection of corrosion data from one metal surface and deposits from another are recognized. Nevertheless,

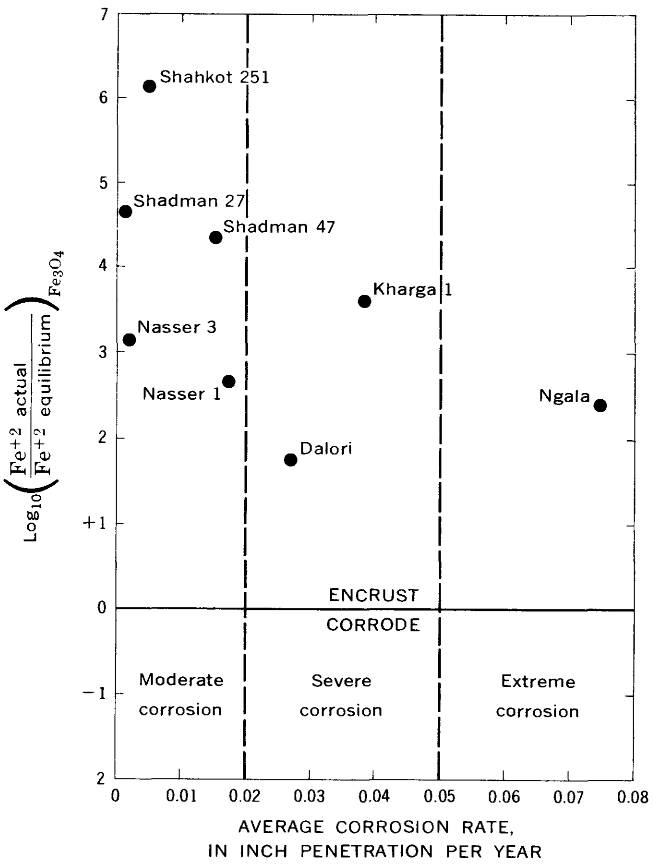

FIGURE 17.—Average corrosion rates plotted against reaction states, Fe_3O_4.

the graphical data in figures 21 and 27 contain strong evidence that there is a high degree of correlation between corrosion rates in deep water wells and saturation with $CaCO_3$ and $Fe(OH)_3$. This indicates the need for more careful studies in natural systems, particularly studies of microenvironments located as closely as possible to the points at which corrosion is occurring. Such work may develop this type of analysis into a more useful tool for predicting the behavior of natural ground-water systems in terms of encrustation and corrosion.

The behavior of the solids considered thus far has been discussed in terms of corrosion and corrosion inhibition. Of equal importance to the operator of a water well is the problem of encrustation or fouling of well screen and casing surfaces. Whether or not corrosion inhibition results, serious losses of well screen transmissibility may result from accumulations of various solids. The observations made on Shadman well 34 show that $Fe(OH)_3$, $CaCO_3$, $FeCO_3$, Mn_3O_4, Fe_3O_4, FeS (both forms), Fe_3S_4, $Cu(OH)_2$(?) and $Mn(OH)_2$(?) all may form more or less troublesome deposits. In the wells reported here, the well yield apparently remains relatively constant until a major part of the screen is plugged. Periodic specific capacity observations in such

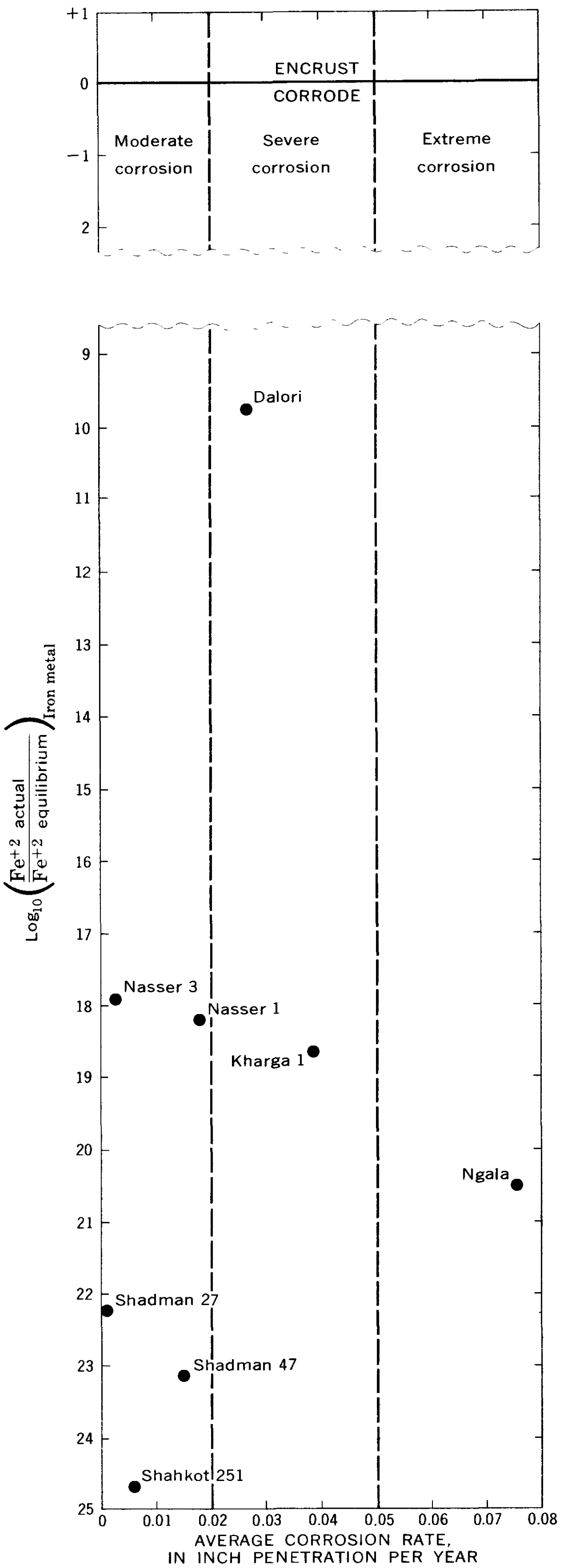

FIGURE 18.—Average corrosion rates plotted against reaction states, iron metal.

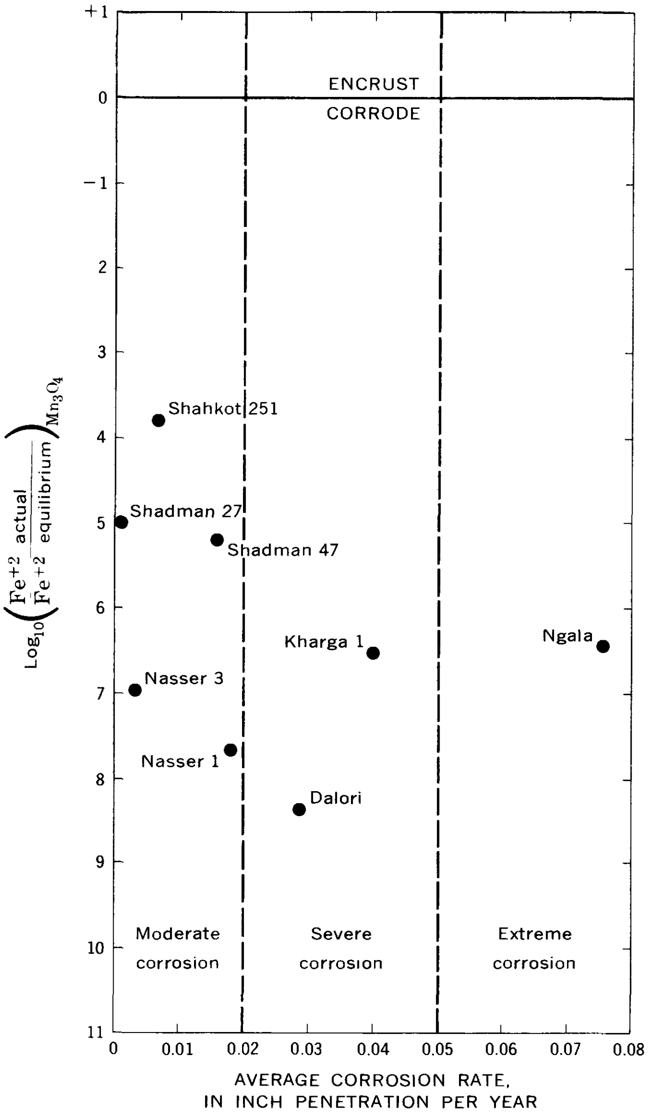

FIGURE 19.—Average corrosion rates plotted against reaction states, Mn_3O_4.

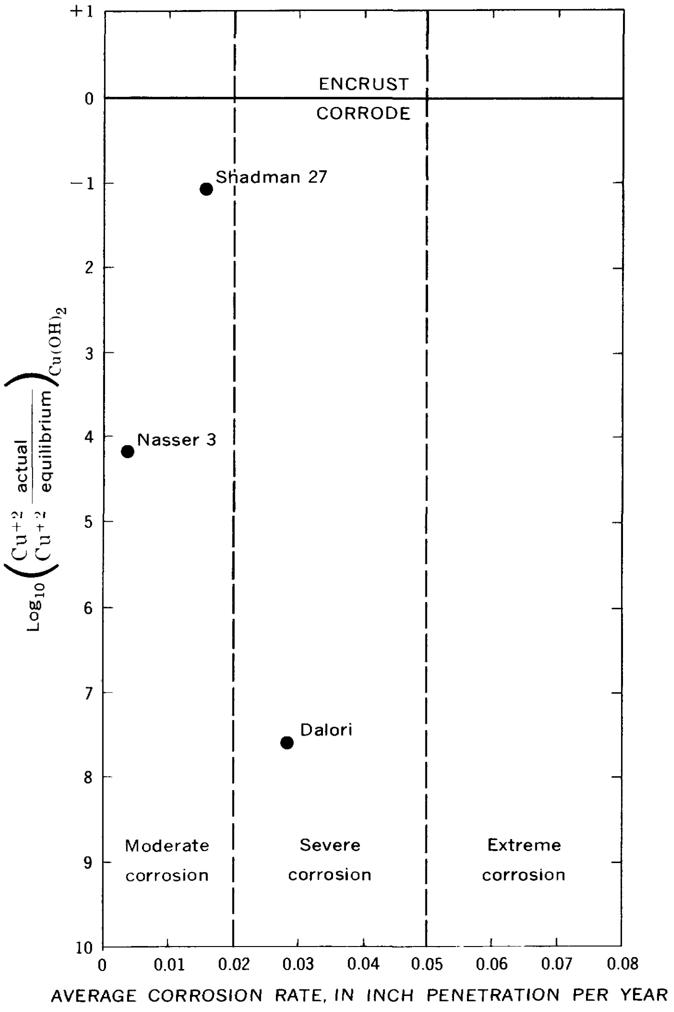

FIGURE 20.—Average corrosion rates plotted against reaction states, $Cu(OH)_2$.

cases do not give sufficient early warning of encrustation or fouling problems. By the time the yield is obviously affected as indicated by conventional capacity tests such extensive and impermeable deposits may have formed as to make physical or chemical cleaning impracticable or at best, only partly effective in restoring expected performance. Much more study of the reaction rates will be needed before reliable predictions can be made of the probability of encrustation and the extent of encrustation at any point in time after start of operation. The nature and extent of encrustation varies locally even in the same well as shown in figure 4.

Chemical cleaning processes for water-well screens have not yet been perfected. However, from the type of data and data analysis reported here, predictions can be made of the mineralogic nature of encrustants likely to form and the best chemical cleaning solution for removing them with minimum damage to well parts. Well-screen materials should be chosen on the basis of resistance to attack by chemical cleaning solutions thought to be required, as well as their corrosion resistance to the natural environment.

If, as the results of this study seem to show, corrosion problems may be separated from encrustation problems on the basis of chemical equilibrium studies, more effective design may be possible. If, for a particular well location, corrosion is expected to be relatively moderate but fouling of the screen is predicted, construction materials should be chosen to resist whatever corrosion is expected to result from periodic chemical or other type of cleaning; conversely, if the environment is known to be corrosive to steel, a more corrosion-resistant construction material should be selected. Fortunately, materials now are available, some at little more than the cost of mild steel, which will resist corrosion by either the aqueous environment or chemical descaling solutions. Stainless steel and rein-

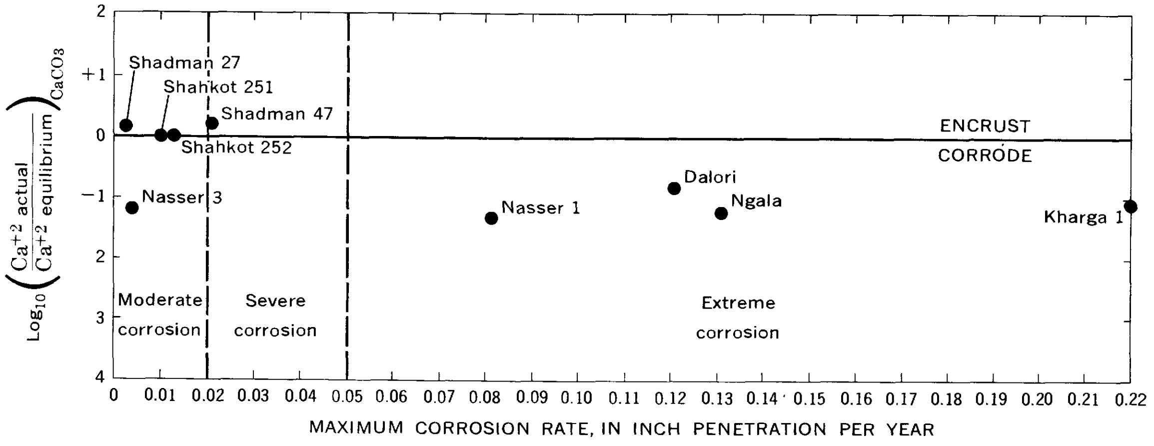

FIGURE 21.—Maximum corrosion rates plotted against reaction states, $CaCO_3$.

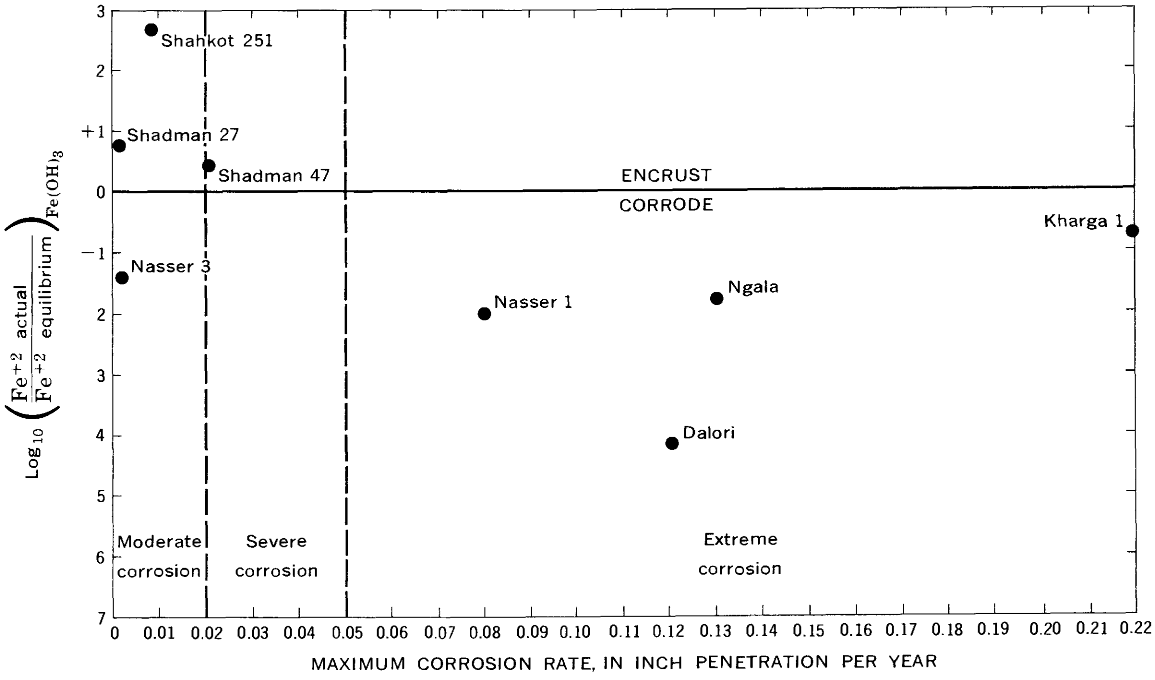

FIGURE 22.—Maximum corrosion rates plotted against reaction states, $Fe(OH)_3$.

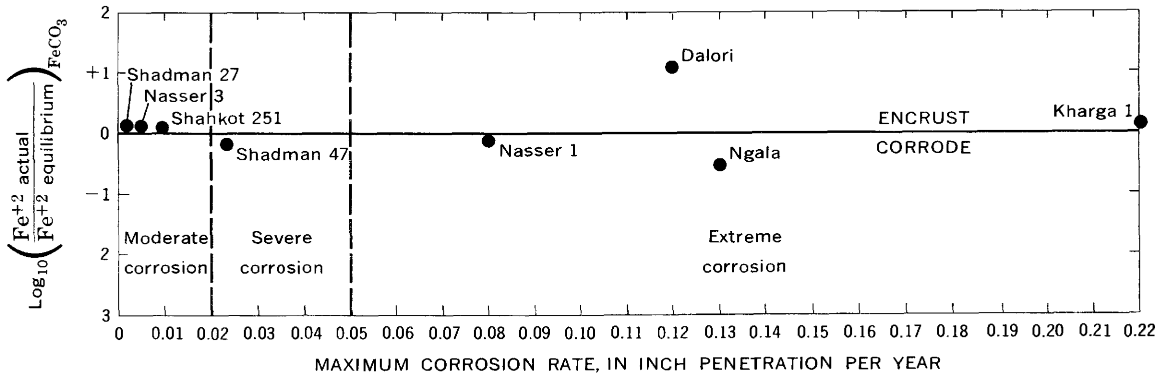

FIGURE 23.—Maximum corrosion rates plotted against reaction states, $FeCO_3$.

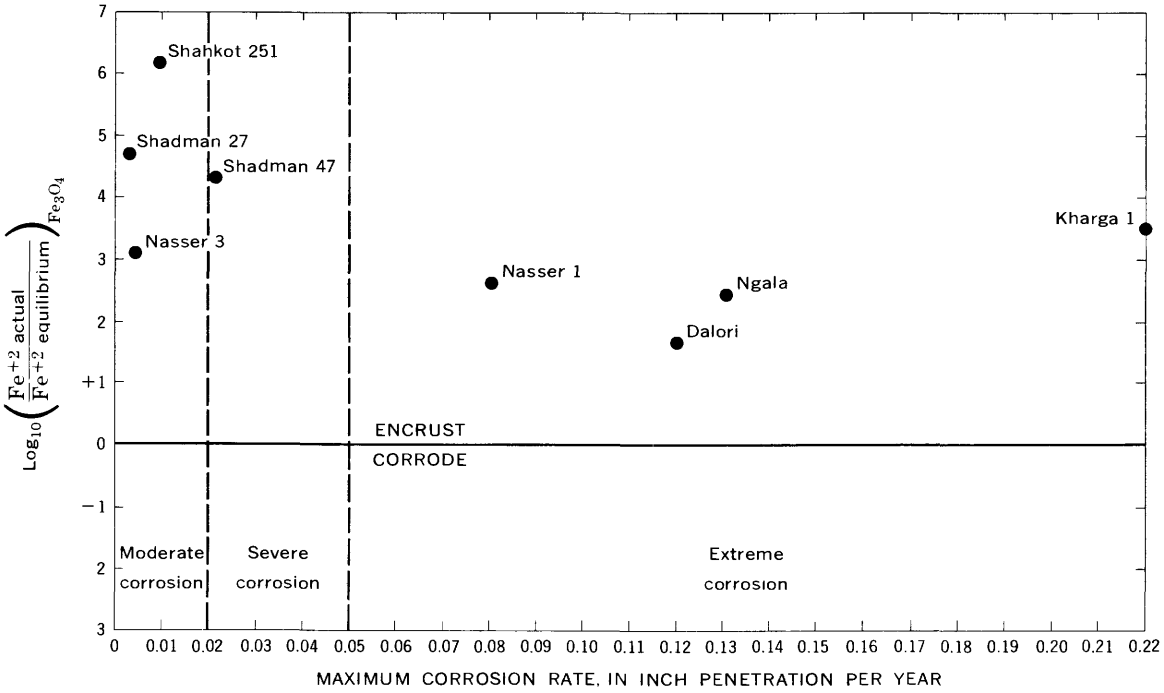

FIGURE 24.—Maximum corrosion rates plotted against reaction states, Fe_3O_4.

forced plastics are examples. The fact that such relatively inert materials have been found to reduce mineral encrustation as well as corrosion (for example, in plastic wells of West Pakistan) supports the suggestion earlier in this paper that catalytic effects of corroding surfaces have a marked bearing on encrustation processes.

SUMMARY

The properties of a number of ground-water samples have been determined by direct measurement in the field of unstable properties such as pH, *Eh*, and the concentrations of HCO_3^-, dissolved oxygen, and iron in the well-water samples. The field determinations have been supplemented by laboratory analyses of specially treated samples, such as precipitation of sulfides for H_2S and acidification for Ca^{+2} and Mn^{+2}. More stable constituents, such as Mg^{+2}, Na^+, K^+, Cl^-, SO_4^{-2}, and copper, were determined in the laboratory on untreated water samples. The data thus obtained should give reliable information on the properties of the water as it comes from the well, with a minimum of uncertainties.

Appropriate thermodynamic and physical chemical arguments were used to analyze the observed data. All the data were analyzed for the conditions found in the field. There was no attempt to reduce the observations to any artificial standard set of conditions. The results of the data analysis, then, give the properties of the water under field conditions and do not involve any assumption as to how the waters should behave. The results of the data analysis should be of interest to the geochemist, because the results show the behavior of a number of geologically important phases in the mixture of natural solutions represented by the discharge of a well.

Data were also obtained on the corrosion resistance of mild steel in a number of wells by means of wire probes. The comparison of physical chemical behavior of various solids leads to an understanding of the conditions under which either corrosion attack or mineral encrustation of the well screen leads to troublesome problems in the withdrawal of ground waters.

Quantitative considerations show that in all 39 wells studied in Egypt, Nigeria, and Pakistan, the waters all were unsaturated with (potentially corrosive to) mild steel (iron metal). The only phases that appear from these observations to inhibit corrosion are calcite, $CaCO_3$, and "limonite," $Fe(OH)_3$. Calcite has long been known as a relatively effective corrosion inhibitor, if properly controlled; thus the results in respect to this mineral are not surprising. It was not possible to show from the results of this study that $Fe(OH)_3$ alone is an effective corrosion inhibiting phase, and further work in this area is needed to determine the effect of the

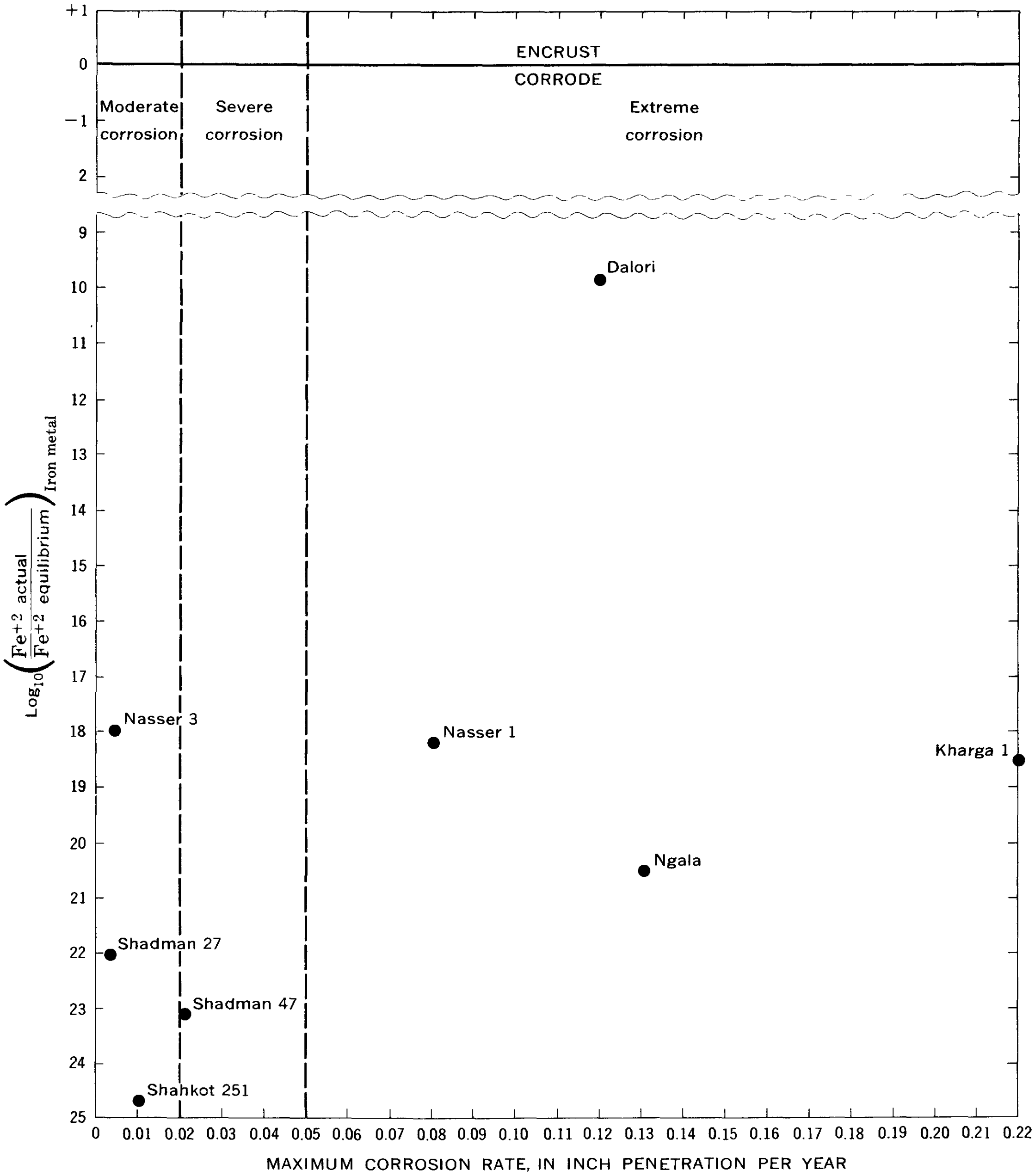

FIGURE 25.—Maximum corrosion rates plotted against reaction states, iron metal.

solubility of $Fe(OH)_3$ on the corrosiveness of ground water on mild steel. None of the other 28 solids considered appears to affect corrosion.

Despite the failure of all but two of the solids to inhibit corrosion, a number of solids apparently are capable of causing troublesome encrustations on well screens: calcite; limonite; magnetite, Fe_3O_4; siderite, $FeCO_3$; hausmannite, Mn_3O_4 (tetragonal); a manganese spinel, Mn_3O_4 (isometric); greigite, Fe_3S_4; mackinawite, FeS (tetragonal); smythite, Fe_3S_4 (rhombohedral); copper hydroxide, $Cu(OH)_2$; and manganese hydroxide, $Mn(OH)_2$. All were at least tentatively identified in the crusts studied and thus are potentially troublesome encrustants.

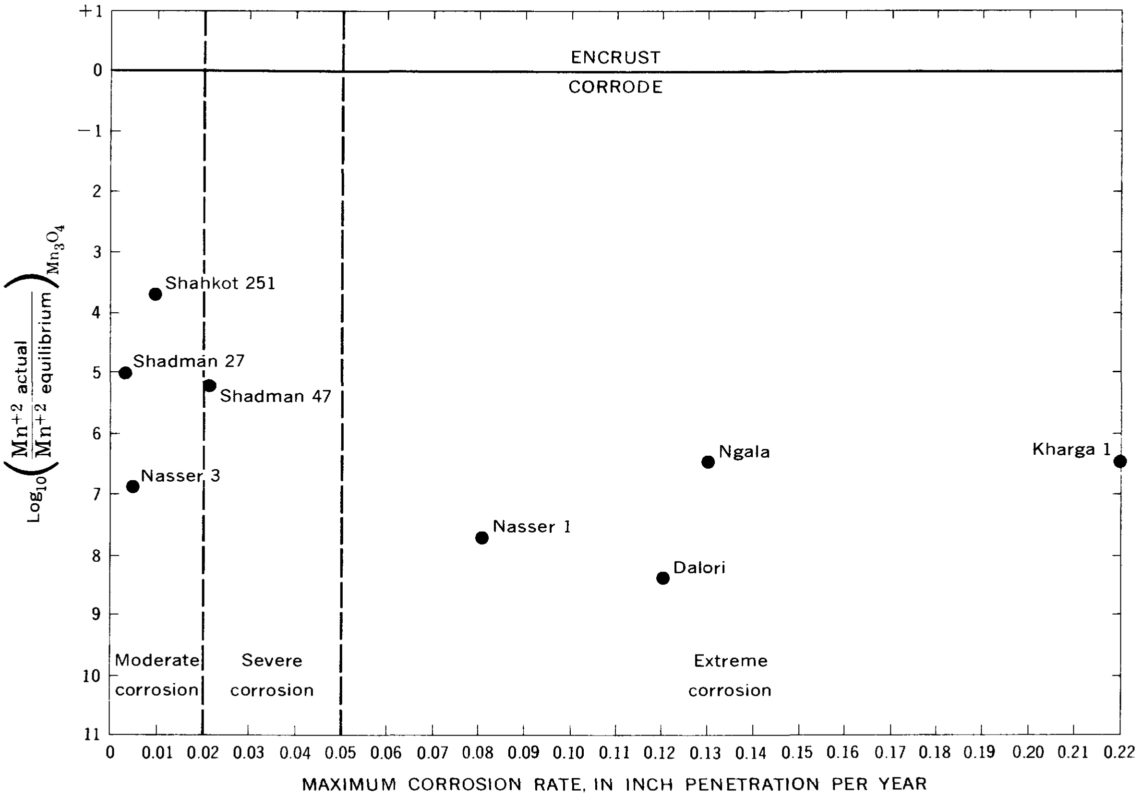

FIGURE 26.—Maximum corrosion rates plotted against reaction states, Mn_3O_4.

Of geochemical interest is the observation that only three solids of the 29 considered exhibited behaviors even approximately predictable from equilibrium models. Calcite apparently precipitates from solutions only slightly supersaturated, and calcite is a stable phase in the waters studied. Both siderite and limonite, as illustrated by $Fe(OH)_3$, may also precipitate from solutions only slightly supersaturated with the appropriate solid phase, but neither siderite nor limonite was a stable solid in any of the waters sampled.

CONCLUSIONS

The results of this study show that equilibrium considerations are useful in establishing a reference for the actual properties and probable effects of naturally occurring ground-water solutions. The detailed physical chemical calculations necessary, when performed on reliable data on the properties of such natural aqueous solutions, are useful in understanding the nature and predicting behaviors of such solutions in water wells and other environments.

The practical results of the study are that the corrosiveness of natural waters upon mild steel may be predicted on the basis of rapid and inexpensive field measurements coupled with laboratory analyses made on appropriately treated water samples. The same data yield useful information on potential encrustation problems that may occur in water wells.

Knowledge of the corroding and encrusting potentials of the ground water simplifies selection of materials and types of construction of wells to minimize the adverse effects stemming from the nature of the water being handled.

Further work is required to establish certain microenvironmental processes within water wells. Local conditions not accurately represented by the bulk discharge from the well may cause problems not otherwise anticipated.

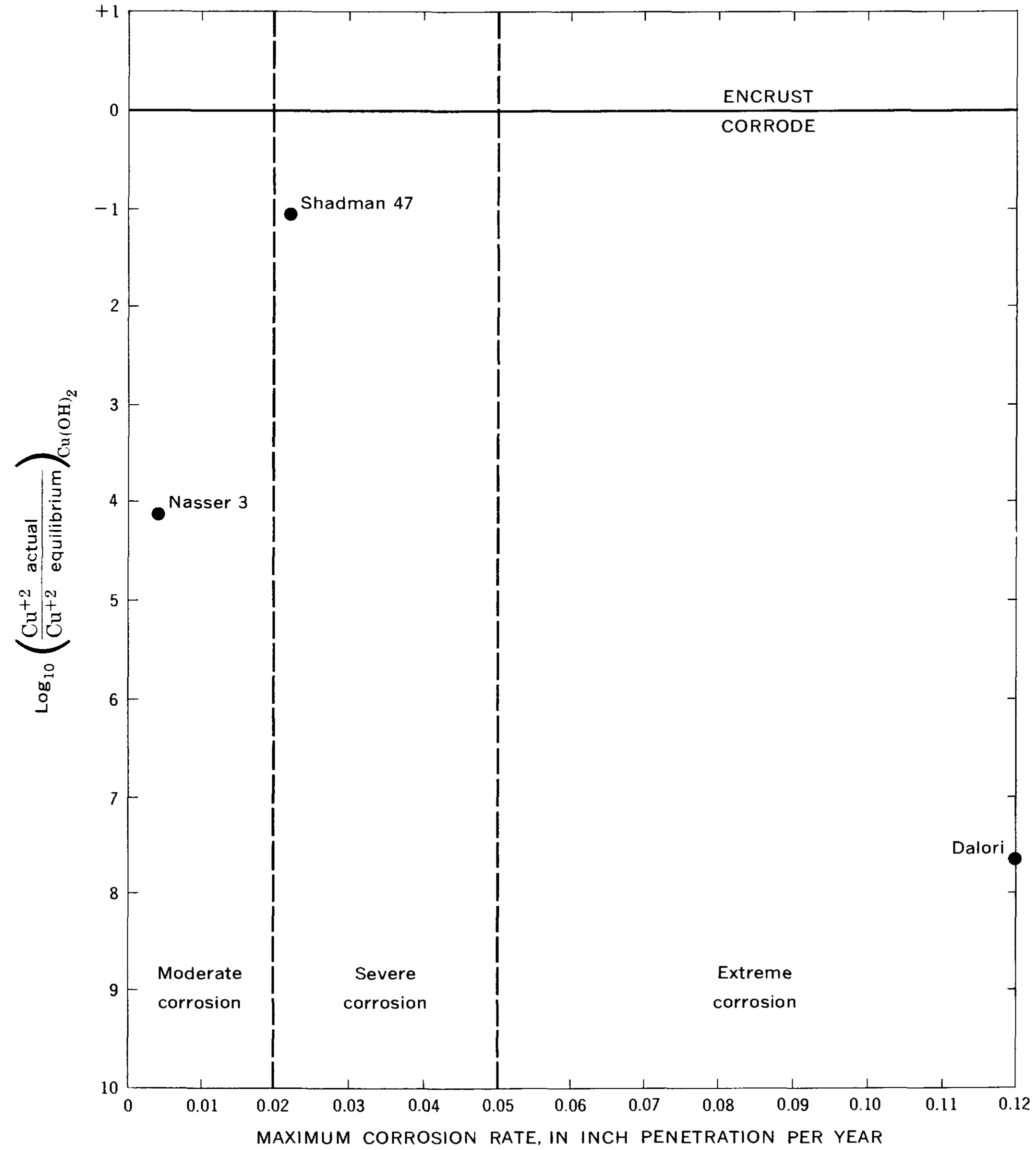

FIGURE 27.—Maximum corrosion rates plotted against reaction states, $Cu(OH)_2$.

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APPENDIX 1

DIGITAL COMPUTER PROGRAM FOR CONSTITUENT ANALYSIS

The listing of the computer program is in ALGOL 60 (extended ALGOL for the B5500). Some translation may be necessary if individual compilers cannot accept this version of ALGOL 60.

The construction of the program is not for efficient use of computation time but for a logical flow of the chemical arguments. The chemical arguments are sufficiently involved that a segregation of types of arguments is not possible. For example, the distribution of copper species involves oxidation potentials. The distribution of the copper species is necessary for considerations of mass-action reactions of copper species not involving oxidation. Similarly, the distribution of manganese species involves only mass-action reactions but the distribution must be known before oxidation reactions involving manganese species may be considered. Mass-action and oxidation reactions are both necessary in the assignment of species. As far as possible, however, the mass-action and oxidation reactions are separated.

The program is open ended in that other species and reactions involve only extensions of arrays already included. If the program is greatly extended, the allowable block size may be exceeded. Three nested blocks are in the listed program and provide for some increase in each.

The exponential nature of some arguments leads to the extensive use of write statements. If an error in data punching is made, the exponential overflow error is quickly found to be after the last write statement. It is urged that write statements be used before and after each logarithmic assignment statement or exponentiation.

All the reactions listed are the same in sequence as the reactions given in the data analysis and results. The identifiers used are in the following table.

Identifier (ALGOL program)	Algebraic notations (data analysis)	Significance
MI	m	Molality.
PPM	ppm	Parts per million parts.
GFW	GFW	Gram formula weight.
MEQ		Milliequivalents per liter.
LOGGAMMA	$\log \gamma_i$	Log_{10} activity coefficient.
DHA	a_o	Effective distance of nearest approach (Debye-Hückel).
GAMMA	γ	Activity coefficient.
ALFA	α	Activity (molal).
AP	AP	Activity product.
LOGEAP	$\ln (AP)$	Natural logarithm of the activity product.
EHTC	EhTC	*Eh* calculated from the composition and temperature of the solution.
CREH	CR	Cation ratio; cation (actual)/ cation (eq) based on *Eh* measurements.
MCATEQ	m_{eq}	Molality of cation at equilibrium with the solids involving oxidation reactions, all other properties of the solution held constant.
PPMCATEQ	ppm_{eq}	Parts per million of cation in equilibrium with solids involving oxidation reactions, all other properties of the solution held constant.
LOGEKTO	$\ln K_{25^\circ\text{C}}$	Natural logarithm of the equilibrium constants at 25°C.
CR	$\alpha_{\text{actual}}/\alpha_{\text{eq}}$; $m_{\text{actual}}/m_{\text{eq}}$; $\text{ppm}_{\text{actual}}/\text{ppm}_{\text{eq}}$.	The ratio of the actual cation concentration or activity to the equilibrim concentration or activity of the cation in equilibrium with the solid phase undergoing mass-action reactions, all other properties of the solutions held constant.
DELMU	$\Delta\mu_{\text{R}}$	The actual chemical potential found for hydrolysis reactions.
DELMUEH	$\Delta\mu_{\text{R}}$	The actual chemical potentials found for oxidation reactions.
N	n	Number of electrons in oxidation reactions.
Z	z	Ionic charge.
ID, PAGE1, PAGE2, PAGE3.	None	Printout arrays.
I	None	Array member.
FLAG1, FLAG2, FLAG3	None	Identifiers for punching errors indicating options not selected.
MU	Γ[1]	Ionic strength.
MUHALF	$\Gamma^{1/2}$	Square root of the ionic strength.
T	T	Temperature, degrees Kelvin.
TEMP	t	Temperature, degrees centigrade.
D	D	Dielectric constant.
DTHALF	$(DT)^{1/2}$	Square root of the temperature (°K) times the dielectric constant.
DT3HALF	$(DT)^{3/2}$	Cube of the square root of the temperature (°K) times the dielectric constant.
A	$A^* d_w{}^{1/2}(DT)^{-3/2}$	See "Data analysis."
B	$B^*(d_w)^{1/2}(DT)^{-1/2}$	See "Data analysis."
K2HCO3	K_{HCO_3}	Equilibrium constant for the dissociation of HCO_3.

---

[1] Both chemical potentials and ionic strengths are commonly designated "μ"; upper case gamma (Γ) has been used for ionic strength in algebraic notation. The authors regret the inconsistency.

Identifier (ALGOL program)	Algebraic notations (data analysis)	Significance
F	$\mathfrak{F}$	Volt equivalent per gram mole.
EHM	Ehm	Measured *Eh* oxidation potential.
R	R	Gas constant.
SUM1, SUM2, DIFF, SUM	None	Used in copper species distribution.
ALFACO3	$\alpha_{CO_3}{}^{-2}$	Activity (molal) of $CO_3{}^{-2}$.
LOGALFACO3	$\log_{10}\alpha_{CO_3}{}^{-2}$	Base 10 logarithm of the activity (molal) of $CO_3{}^{-2}$.
DUM	None	$RT/\mathfrak{F}$ or $\mathfrak{F}/RT$ used for efficient coding.
LOGKIH2CO3	$\log_{10}K_{H_2CO_3}$	Base 10 logarithm of the equilibrium constant for the dissociation of H_2CO_3.
MCO2AQ	$m_{CO_2(aq)}$	Molality of $CO_{2(aq)}$.
LOGPCO2	$\log_{10}P_{CO2}$	Base 10 logarithm of the partial pressure of $CO_{2(g)}$ in equilibrium with the solution.
PCO2	P_{CO_2}	Partial pressure of $CO_{2(g)}$ in atmospheres that would be in equilibrium with the solution.
PPMCO2AQ	$ppm_{CO_2(aq)}$	Parts per million of $CO_{2(aq)}$.
PH	pH	pH.
EOFE3S4	$E°_{Fe3S4}$	The standard oxidation potential calculated from the properties of the solution assuming the solution in equilibrium with greigite for which no $\Delta G°$ values are available. $\Delta G°$ data so obtained are about -52 kcal.
C	$\log_{10}e$	Base 10 logarithm of *e*, the base of natural logarithms.
E	ln 10	Natural logarithm of 10.
LNKHS	$\ln K_{H_2S(aq)}$	Natural logarithm of the equilibrium constant for the dissociation of $H_2S_{(aq)}$.
K1H2CO3	$K_{H_2CO_3}$	Equilibrium constant for the dissociation of H_2CO_3.
LOGMI13	$\log_{10}m_{H_2S}$	Base 10 logarithm of the molality of $H_2S_{(aq)}$.
POW	None	Exponents used for ease of coding exponentiation.
LOGMSO4	$\log_{10}m_{SO4(eq)}$	Base 10 logarithm of the activity of $SO_4{}^{-2}$ (molal) at equilibrium with $H_2S_{(aq)}$ at the measured *Eh*, pH, and other actual properties of the solution.
DENS	d_w	Density of water.
DELT	$374.11-t$ (°C)	A term from Keenan and Keys (1936) used in calculating the density of water.
LOGACTFEPYSO4	$\log_{10}\alpha_{Fe}{}^{+2}{}_{eq}$	Base 10 logarithm of the activity (molal) of Fe^{+2} in equilibrium with pyrite at the pH, *Eh*, and $SO_4{}^{-2}$ activity found in the solution.
G, H, J, DIFI, D1F2	None	Used in copper species distribution.
DENSHALF	$d_w{}^{1/2}$	Square root of the density of water.

In addition to the listing and glossary, "Appendix 1" also contains a test case (p. D47) with the actual printout (p. D42–D46) from the test case. The input data are exactly the data given in the printout with the following exceptions:

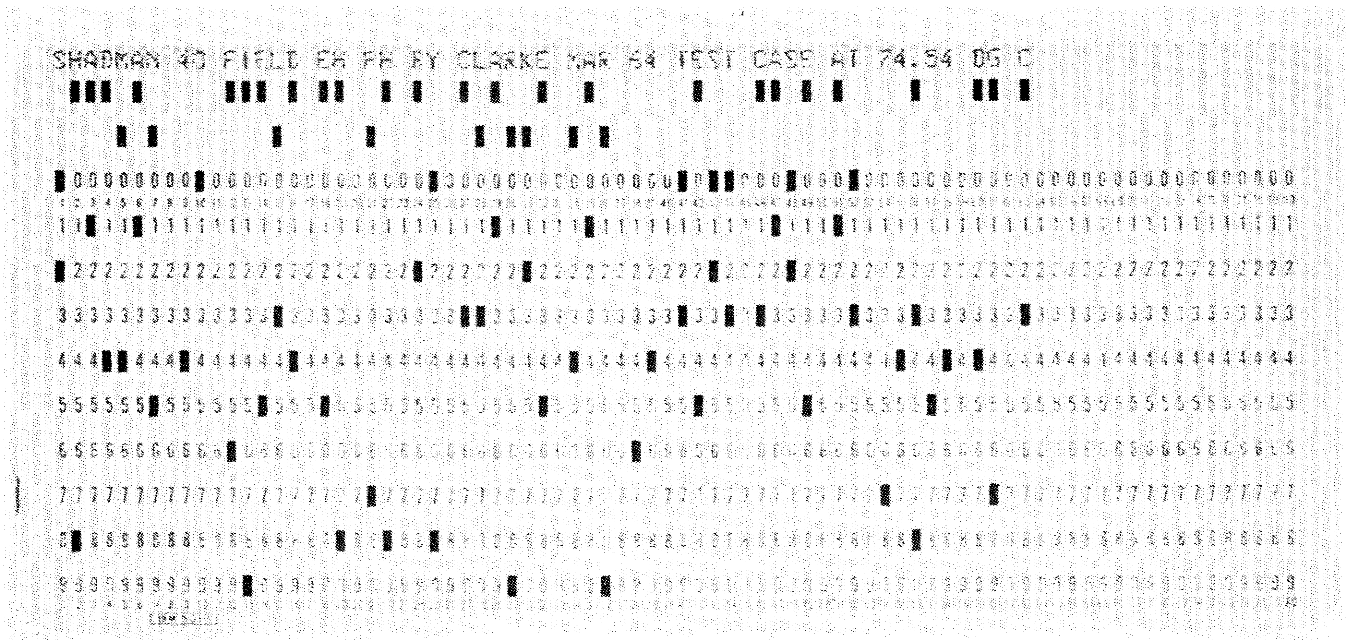
MN 2 The printed Mn^{+2} data are not the Mn^{+2} input data. Within the program the total Mn is distributed among Mn^{+2}, $MnHCO_3{}^{+}$, and $MnSO_4{}^{\circ}$ aqueous species. The computed Mn^{+2} is printed.

CU1, CU2, CU2OH2, CUTOT. The distribution of the copper among Cu^{+1}, Cu^{+2}, and $Cu_2(OH)_2{}^{+2}$ is computed from the properties of the solutions and the total copper (CUTOT). CUTOT is thus input data but CU1, CU2 and CU2OH2 are computed results.

HS, H2S, H2STOT. The distribution of the sulfide species, $H_2S_{(aq)}$ and HS^-, is computed from the total aqueous sulfide analysis (H2STOT) and the properties of the solution. HS and H2S are computed and H2STOT is the total sulfide input data.

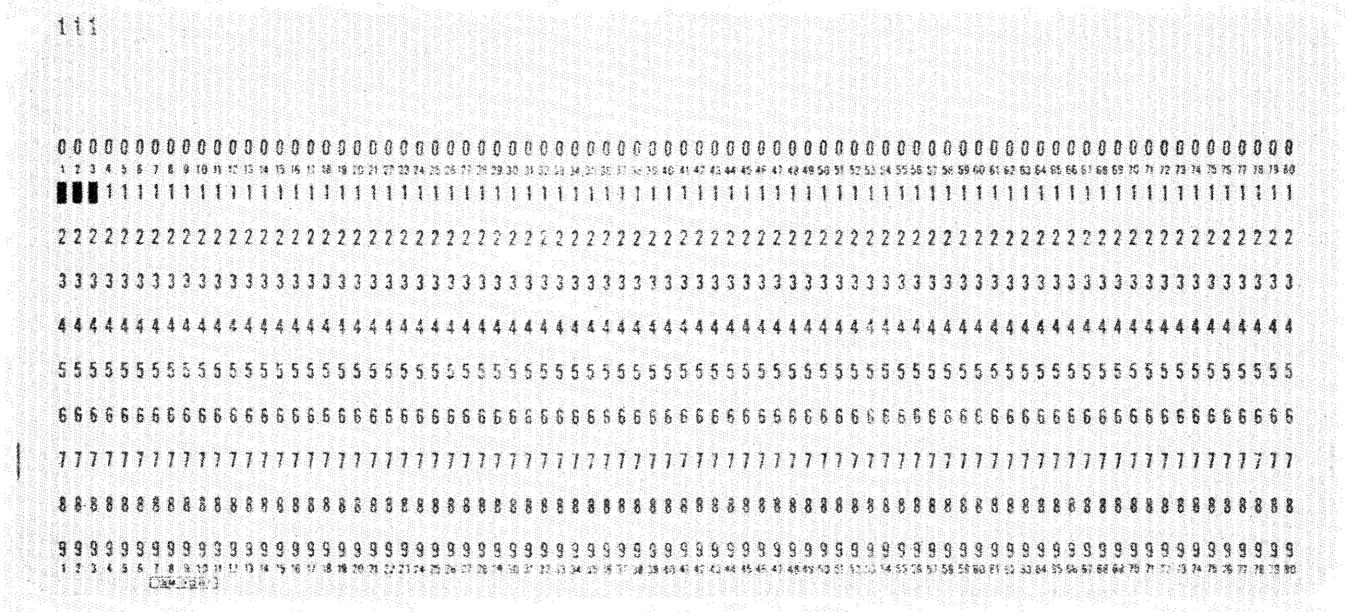
SO^4 The sulfate concentration is high to test the distribution of the sulfate species.

The input is on four punch cards which are reproduced on pages D40–D41.



SHADMAN 40 FIELD EH PH BY CLARKE MAR 64 TEST CASE AT 74.54 DG C

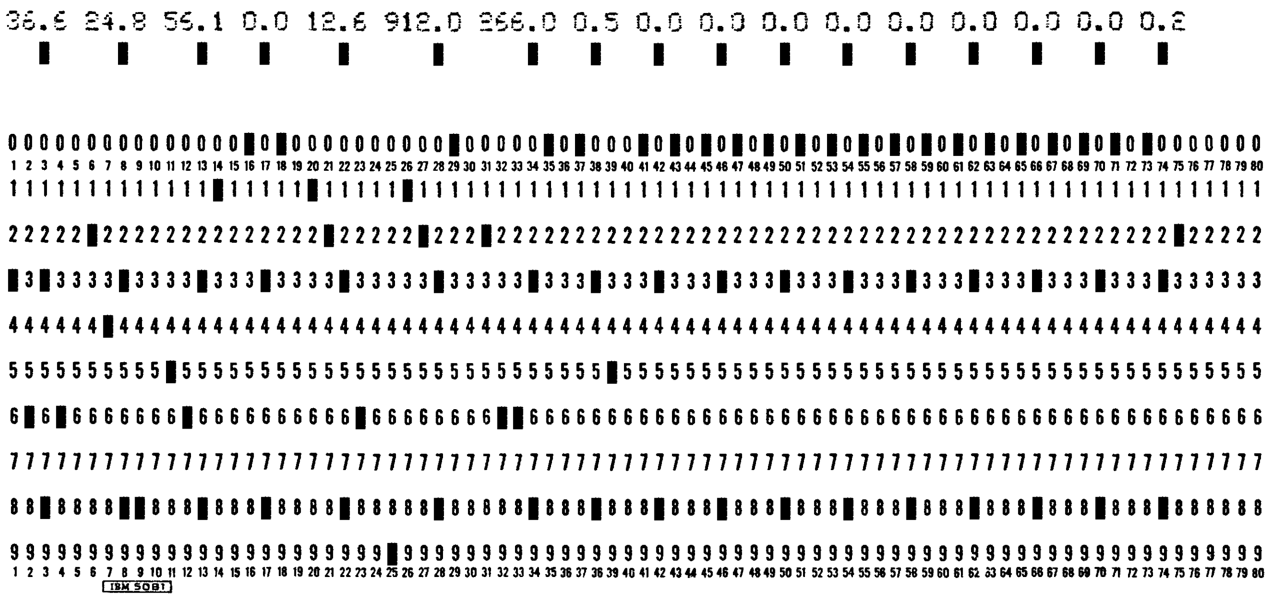
Card 1



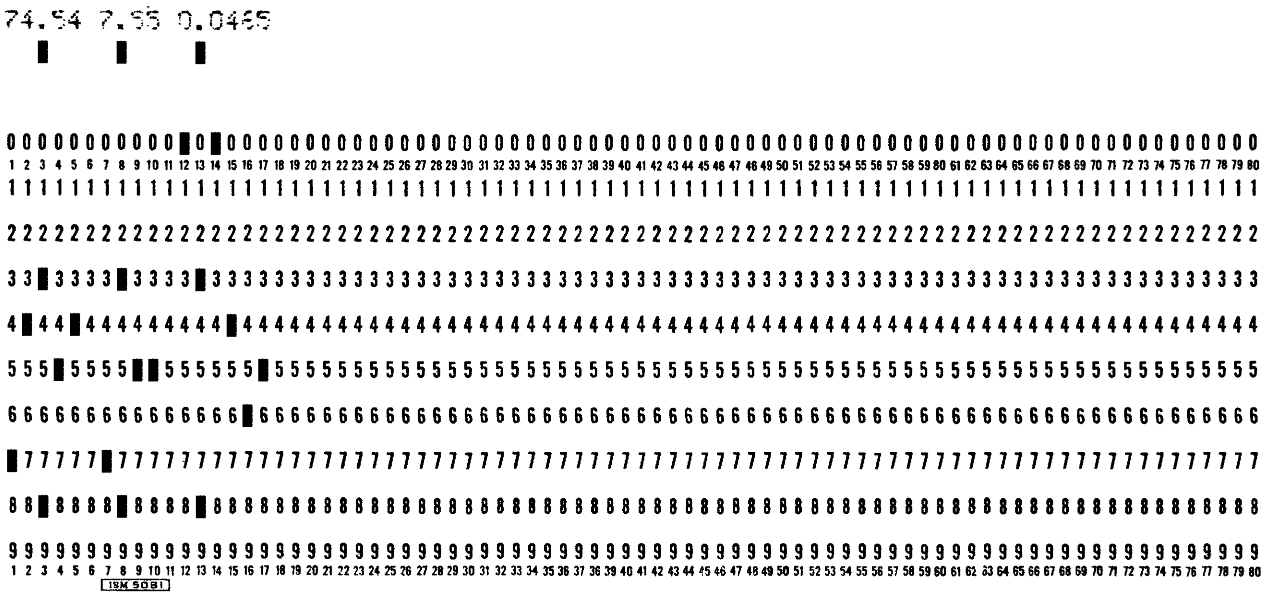
111

Card 2

Sample cards in Stanford version ALGOL 60. Shadman well 40, West Pakistan, test case at 74.54 DG C. Field *Eh*, pH, Fe^{+2}, HCO_3, and S by F. E. Clarke (U.S. Agency for International Development) and West Pakistani (Water and Soils Investigation Division) scientists, March 1964; other chemical data by U.S. Geological Survey laboratories July 1964.


36.6 24.8 55.1 0.0 12.6 912.0 266.0 0.5 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.2

Card 3


74.54 7.55 0.0465

Card 4

Sample cards—Continued.

Printout from test case on page D47

```
                     STANFORD B5500 ALGCL -- 07/05/66 VERSION       254/67     1668
BEGIN REAL ARRAY MI,PPM,GFW,MEQ[0:16],LOGGAMMA,DHA,GAMMA,ALFA[0:14],AP,L.     0010   0001   0000
OGEAP[0:18],EHTC,CREH,MCATEQ,PPMCATEQ[0:13],LOGEKTO,DH,EOT,DHO,E0298,LOG.     0020   0002   0012
K,APKRAT,LOGME,ME,PPMEQ,LOGEKT,KT,CR,DELMU[0:18],DELMUEH[0:13];INTEGER A.     0030   0002   0018
RRAY N[0:13],Z[0:16];ALPHA ARRAY ID[0:12],PAGE1[0:16],PAGE2[0:18],PAGE3[.     0040   0002   0023
0:13];INTEGER I,FLAG1,FLAG2,FLAG3;REAL MU,MUHALF,T,TEMP,D,DTHALF,DT3HALF.     0050   0002   0032
,A,B,K2HCO3,F,EHM,R,SUM1,SUM2,DIFF,SUM,FACTOR,ALFACO3,LOGALFACO3,DUM,LOG.     0060   0002   0033
K1H2CO3,MCO2AQ,LOGPCO2,PCO2,PPMCO2AQ,PH,EOFE3S4,C,E,LNKHS,K1H2CO3,LOGMI1.     0070   0002   0033
3,POW,LOGMSO4,DENS,DELT,LOGACTFEPYSO4,G,H,J,DIF1,DIF2,DENSHALF;LABEL STA.     0080   0002   0033
RT,EOF,LOOP1,LOOP2,LOOP3,CONT;FORMAT IG(13A6,/3I1),HEADF(13A6),FORM1(X3,.     0090   0002   0033
"PH",X4,"EH MEAS",X5,"T",X6,"ION STRENGTH  PCO2 ATM",X4,"MCO2 AQ",X4,"PP.     0100   0004   0033
M CO2 AQ   EO FE3S4",X2,"LOGACTSO4 EQ   LOG ACT FE PY SO4"/F6.2,F10.4,F8.     0110   0004   0033
.2,F13.5,F14.7,F11.6,F10.2,F12.3,2F14.4,//X4,"ION",X9,"PPM",X8,"GAMMA",X.     0120   0004   0033
6,"MOLALITY",X5,"ALPHA"),FORM2(I2,X2,A6,F12.3,F12.6,X1,2E12.4),FORM3(/X3.     0130   0004   0033
,"PHASE",X8," AP",X10,"KT",X8," AP/K",X7,"  CR   ",X4,"MOL CAT EQ"X1,"PP.     0140   0004   0033
MCATEQUIL",X4,"DEL MU"),FORM4(I2,X5,A6,E11.4,5E12.4,F12.5),FORM5(/X3,"PH.     0150   0004   0033
ASE",X8,"EOT",X6,"EH T CALC      CR      MOL CATEQUIL PPM CATEQUIL",X4,".     0160   0004   0033
DEL MU"),FORM6(I2,X1,A6,F11.4,F15.4,X1,3E12.4,F12.6),ERRFM1("REDUCTION C.     0170   0004   0033
ANNOT ","PROCEDE   CU1=",E11.4,"  CU2=",E11.4,"  CU2OH2=",E11.4/),ERROR1.     0180   0004   0033
("CONCENTRATION UNITS NOT SPECIFIED, FLAG1 IS MISSING"),ERROR2("FLAG2 MI.     0190   0004   0033
SSING, EHM NOT SPECIFIED"),ERROR3("FLAG3 IS MISSING. DO YOU WANT CALCULA.     0200   0004   0033
TED  EH VALUES?");DEFINE IUP=FOR I←0STEP 1UNTIL#;LIST ERR1(MI[10],MI[11].     0210   0004   0033
,MI[14]);FILL GFW[*]WITH 40.08,24.312,22.9898,39.102,35.453,96.0616,61.0.     0220   0002   0038
1732,55.847,55.847,54.938,63.54,63.54,33.07197,34.07994,161.09474,63.54,.     0230   0002   0045
34.07994;FILL DHA[*]WITH 6,8,4,3,3,4,4,6,9,6,3,6,3.5,0,10;FILL Z[*]WITH .     0240   0002   0045
2,2,1,1,1,2,1,2,3,2,1,2,1,1,2,2,1;FILL N[*]WITH 2,2,1,8,2,2,2,2,2,2,14,1.     0250   0002   0047
,2,1;FILL E0298[*]WITH-0.44,0.981353,1.056808,0.303339,1.228968,1.820468.     0260   0002   0050
,1.443408,-0.1400694,0.337,0.7278838,0.366683,0.153,0.46656,1.885082;FIL.     0270   0002   0052
L DHO[*]WITH-21.0,68.368,28.951,65.768,65.734,101.768,79.451,-2.72,15.39.     0280   0002   0052
,50.451,134.256,2.99,0.0,-46.251;FILL LOGEKTO[*]WITH-3.865777,18.1640871.     0290   0002   0054
6,21.185808,-41.36621,-13.33847,-34.92704,-64.24955,-24.9548,30.5717126,.     0300   0002   0055
-24.545152,-18.214731,-39.14395,0.0,0.0,0.0,0.0,35.2541,-10.19803,-10.62.     0310   0002   0055
014;FILL DH[*]WITH-3.677,-15.827,-15.144,0.0,0.0,17.59,34.4,-1.03,-21.83.     0320   0002   0055
4,-4.63,-6.04,0.0,0.0,0.0,0.0,0.0,-23.134,-4.25,-0.244;C←2.30258509;F←23.     0330   0002   0057
.0603;R←0.00198719;E←0.43429448;FILL PAGE1[*]WITH"CA     ","MG     ","NA  .     0340   0002   0058
 ","K     ","CL     ","SO4    ","HCC3  ","FE 2  ","FE 3  ","MN 2  ","CU 1.     0350   0002   0062
 ","CU 2  ","HS     ","H2S    ","CU2DH2","CUTOT ","H2STOT";FILL PAGE2[*]W.     0360   0002   0062
ITH"CU2O  ","CUO    ","CU(OH2","AZURIT","MALACH","CUS    ","CU2S  ","MNCO3.     0370   0002   0062
 ","FE(OH2","FECO3 ","MGCO3 ","DOLCMI","CACO3 ","FES    ","CUFES2","BORNI.     0380   0002   0064
T","MN(OH2","ANHYDR","GYPSUM";FILL PAGE3[*]WITH"FE MET","FE3O4 ","FE(OH3.     0390   0002   0064
","H2S   ","MNO2  ","MN3O4 ","MN2O3 ","PY H2S","CU MET","FE2O3 ","PY SO4.     0400   0002   0065
","CUDIST","CUDIST","MN(OH3";START:READ(CARDFIL,IG,IUP 12DO ID[I],FLAG1,.     0410   0002   0065
FLAG2,FLAG3)[EOF];WRITE(PRINFIL[PAGE]);WRITE(PRINFIL,HEADF,IUP 12DO ID[I.     0420   0002   0080
]);IF FLAG1=1THEN READ(CARDFIL,/,ILP 16DO PPM[I])ELSE IF FLAG1=2THEN REA.     0430   0002   0099
D(CARDFIL,/,IUP 16DO MEQ[I])ELSE IF FLAG1=0THEN BEGIN WRITE(PRINFIL,ERRO.     0440   0002   0119
R1);READ(CARDFIL);READ(CARDFIL);GO TO START END;IF FLAG2=1THEN READ(CARD.     0450   0002   0136
FIL,/,TEMP,PH,EHM)ELSE IF FLAG2=2THEN BEGIN READ(CARDFIL,/,TEMP,PH);EOFF.     0460   0002   0146
3S4←-99.999;LOGACTFEPYSO4←LOGMSO4←C.0END ELSE IF FLAG2=0THEN BEGIN WRITE.     0470   0002   0168
(PRINFIL,ERROR2);READ(CARDFIL);READ(CARDFIL);GO TO START END;IF FLAG3=0T.     0480   0002   0174
HEN BEGIN READ(CARDFIL);READ(CARDFIL);WRITE(PRINFIL,ERROR3);GO TO START .     0490   0002   0184
END;IF FLAG1=1THEN IUP 16DO MI[I]←PPM[I]/(1000.0×GFW[I])ELSE IF FLAG1=2T.     0500   0002   0195
HEN BEGIN IUP 16DO PPM[I]←MEQ[I]×GFW[I]/Z[I];IUP 16DO MI[I]←MEQ[I]/(1000.     0510   0002   0206
.0×Z[I]);END;MU←0.0;DELT←(374.11-TEMP);DENS←(1.0+0.134248 9×DELT*(1/3)-0..     0520   0002   0219
003946263×DELT)/(3.1975-0.3151548×DELT*(1/3)-0.001203374×DELT+7.48908@-1.     0530   0002   0228
3×DELT*4);DENSHALF←SQRT(DENS);IUP 9DO MU←MU+MI[I]×Z[I]*2;MU←MU/2;MUHALF←.     0540   0002   0234
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SQRT(MU);T←TEMP+273.16;TEMP←TEMP-25;IF T≤373.16THEN D←78.54×(1.0-0.00457.      0550   0002   0255
9×TEMP+11.9×1.0@-6×TEMP*2+2.8×1.0@-8×TEMP*3)ELSE D←5321.0/T+233.76-0.929.      0560   0002   0260
7×T+0.001417×T*2+(8.292@-7)×T*3;DTHALF←SQRT(D×T);DT3HALF←DTHALF*3;A←1824.      0570   0002   0278
347.0×DENSHALF/DT3HALF;B←DENSHALF×50.297/DTHALF;IUP 12,14DO LOGGAMMA[I]←.      0580   0002   0286
-A×MUHALF×Z[I]*2/(1.0+DHA[I]×B×MUHALF);LOGGAMMA[13]←0.0;IUP 12,14DO GAMM.      0590   0002   0297
A[I]←10*LOGGAMMA[I];GAMMA[13]←1.0;IUP 8DO ALFA[I]←GAMMA[I]×MI[I];K2HCO3←.      0600   0002   0319
10*(6.498-0.02379×T-2902.39/T);WRITE(<"NO.1">);IF MI[9]>0.0THEN MI[9]←MI.      0610   0002   0332
[9]/(1.0+190.0×GAMMA[9]×ALFA[5]+63.0×GAMMA[9]×MI[6]);PPM[9]←MI[9]×GFW[9].      0620   0002   0341
×1000.0;IUP 13DO EOT[I]←IF DHO[I]=0.0THEN E0298[I]ELSE T×E0298[I]/298.16.      0630   0002   0348
+DHO[I]×(298.16-T)/(298.16×N[I]×F);IF MI[15]≤0OR FLAG2≠1THEN GO TD CONT;.      0640   0002   0358
MI[11]←MI[15];POW←(2.0×PH×C);MI[14]←6.026×(GAMMA[11]×MI[11])*2×EXP(PDW)/.      0650   0002   0373
(GAMMA[14]×10*11);WRITE(<"NO.2">);PDW←(F×(EOT[11]-EHM)/(R×T));MI[10]←EXP.      0660   0002   0380
(POW)×MI[11]×GAMMA[11]/GAMMA[10];WRITE(<"NO.3">);IF MI[11]>MI[10]AND MI[.      0670   0002   0391
11]>MI[14]THEN BEGIN J←MI[11];LOOP1:G←MI[10];H←MI[14];SUM1←G+2×H+J;MI[10.      0680   0002   0399
]←EXP(F×(EOT[11]-EHM)/(R×T))×MI[11]×GAMMA[11]/GAMMA[10];MI[14]←6.026×(GA.      0690   0002   0407
MMA[11]×MI[11])*2×10*(2.0×PH-11.0)/GAMMA[14];SUM2←MI[11]+MI[10]+2×MI[14].      0700   0002   0414
;IF SUM2>1.1×MI[15]THEN BEGIN J←MI[11];MI[11]←MI[11]-0.05×MI[15];GO TO L.      0710   0002   0422
OOP1 END ELSE IF SUM2>1.01×MI[15]THEN BEGIN J←MI[11];MI[11]←MI[11]-0.005.      0720   0002   0429
×MI[15];GO TO LOOP1 END ELSE IF SUM2>1.001×MI[15]THEN BEGIN J←MI[11];MI[.      0730   0002   0440
11]←MI[11]-0.0005×MI[15];GO TO LOOP1 END ELSE BEGIN DIF1←ABS(SUM1-MI[15].      0740   0002   0448
);DIF2←ABS(SUM2-MI[15]);IF DIF2>DIF1 THEN BEGIN MI[11]←J;MI[10]←G;MI[14].      0750   0002   0455
←H END END END ELSE IF MI[10]>MI[11]AND MI[10]>MI[14]THEN BEGIN MI[10]←G.      0760   0002   0462
←MI[15];LOOP2:J←MI[11];H←MI[14];SUM1←G+2×H+J;MI[11]←EXP(F×(EHM-EOT[11])/.      0770   0002   0467
(R×T))×MI[10]×GAMMA[10]/GAMMA[11];MI[14]←(MI[10]×GAMMA[10])*2×10*(2×PH)×.      0780   0002   0475
EXP(2×F/(R×T)×(EHM-EOT[12]));SUM2←MI[10]+MI[11]+MI[14];IF SUM2>1.1×MI[15.      0790   0002   0482
]THEN BEGIN G←MI[10];MI[10]←MI[10]-0.05×MI[15];GO TO LOOP2 END ELSE IF S.      0800   0002   0492
UM2>1.01×MI[15]THEN BEGIN G←MI[10];MI[10]←MI[10]-0.005×MI[15];GO TO LOOP.      0810   0002   0500
2 END ELSE IF SUM2>1.001×MI[15]THEN BEGIN G←MI[10];MI[10]←MI[10]-0.0005×.      0820   0002   0506
MI[15];GO TO LOOP2 END ELSE BEGIN DIF1←ABS(SUM1-MI[15]);DIF2←ABS(SUM2-MI.      0830   0002   0513
[15]);IF DIF2>DIF1 THEN BEGIN MI[10]←G;MI[11]←J;MI[14]←H END END END ELS.      0840   0002   0520
E IF MI[14]>MI[10]AND MI[14]>MI[11]THEN BEGIN MI[14]←H←MI[15];LOOP3:G←MI.      0850   0002   0527
[10];J←MI[11];SUM1←G+2×H+J;MI[11]←SQRT(MI[14]×GAMMA[14])/0.6206×10*(5.0-.      0860   0002   0533
PH)/GAMMA[11];MI[10]←SQRT(MI[14]×GAMMA[14])×EXP(F×(EOT[12]-EHM)/(R×T))/(.      0870   0002   0540
GAMMA[10]×10*PH);SUM2←MI[10]+MI[11]+2×MI[14];IF SUM2>1.1×MI[15]THEN BEGI.      0880   0002   0549
N H←MI[14];MI[14]←MI[14]-0.05×MI[15];GO TO LODP3 END ELSE IF SUM2>1.01×M.      0890   0002   0558
I[15]THEN BEGIN H←MI[14];MI[14]←MI[14]-0.005×MI[15];GO TO LOOP3 END ELSE.      0900   0002   0568
 IF SUM2>1.001×MI[15]THEN BEGIN H←MI[15];MI[14]←MI[14]-0.0005×MI[15];GO .      0910   0002   0576
TO LOOP3 END ELSE BEGIN DIF1←ABS(SUM1-MI[15]);DIF2←ABS(SUM2-MI[15]);IF D.      0920   0002   0582
IF2>DIF1 THEN BEGIN MI[14]←H;MI[10]←G;MI[11]←J END END                  .      0930   0002   0589
                                                  END ELSE BFGIN WRITF(P.      0940   0002   0594
RINFIL,ERRFM1,ERR1);GO TO START END;CONT:LNKHS←C×(103.366829-36.456001×E.      0950   0002   0594
×LN(T)-6003.4/T);WRITE(<"NO.10">);MI[13]←MI[16]/(1.0+EXP(LNKHS)×10*PH/GA.      0960   0002   0599
MMA[12]);MI[12]←MI[16]-MI[13];WRITE(<"NO.11">);PPM[13]←1000×GFW[13]×MI[1.      0970   0002   0610
3];PPM[12]←1000×GFW[12]×MI[12];IF MI[13]>0.0THEN LOGMI13←LN(MI[13])×E;FO.      0980   0002   0619
R I←9STEP 1UNTIL 14DO ALFA[I]←MI[I]×GAMMA[I];ALFACO3←ALFA[6]×K2HCD3×10*P.      0990   0002   0626
H;WRITE(<"NO.12">);LOGALFACO3←E×LN(ALFACO3);DUM←10*(2.0×PH);WRITE(<"NO.1.      1000   0002   0639
3">);AP[0]←DUM×ALFA[10]*2;WRITE(<"NO.14">);AP[1]←ALFA[11]×DUM;AP[2]←AP[1.      1010   0022   0651
];WRITE(<"NO.15">);AP[3]←AP[1]×(ALFA[11]×ALFACO3)*2;WRITE(<"NO.16">);AP[.      1020   0002   0661
4]←ALFA[11]*2×ALFACO3×DUM;WRITE(<"NO.17">);AP[5]←MI[13]×AP[1];AP[6]←MI[1.      1030   0002   0671
3]×AP[0];WRITE(<"NO.18">);AP[7]←ALFA[9]×ALFACO3;AP[8]←DUM×ALFA[7];WRITE(.      1040   0002   0680
<"NO.19">);AP[9]←ALFA[7]×ALFACO3;AP[10]←ALFA[1]×ALFACO3;WRITE(<"NO.20">).      1050   0002   0688
;AP[11]←ALFA[0]×AP[10]×ALFACO3;WRITE(<"NO.21">);AP[12]←ALFA[0]×ALFACO3;A.      1060   0029   0697
P[13]←DUM×ALFA[7]×MI[13];WRITE(<"NC.22">);AP[14]←AP[13]×DUM×MI[13]×ALFA[.      1070   0002   0706
11];WRITE(<"NO.23">);AP[15]←AP[14]×(DUM×MI[13])*2×ALFA[10]*4;AP[16]←ALFA.      1080   0002   0714
[9]×10*(2×PH);AP[18]←AP[17]←ALFA[0]×ALFA[5];WRITE(<"NO.24">);AP[16]←ALFA.      1090   0002   0724
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Printout from test case on page D47—Continued

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[9]×DUM;IUP 18DO LOGEAP[I]←IF AP[I]=0.0THEN 999.9ELSE LN(AP[I]);LOGK1H2C.   1100   0002   0735
03←-3404.71/T-0.032786×T+14.8435;K1H2C03←10*LOGK1H2C03;WRITE(<"NO.25">);.    1110   0002   0748
BEGIN LABEL NEXTCOMP,ENDOFEH;MCO2AQ←ALFA[6]/(K1H2C03×10*PH);TEMP←TEMP+25.    1120   0002   0756
;WRITE(<"NO.26">);LOGPCO2←E×LN(MCO2AQ)-2385.73/T-0.015264×T+14.0184+MU×(.    1130   0035   0004
0.119-0.000833×TEMP+0.00000666×TEMP*2);WRITE(<"NO.27">);PCO2←10*LOGPCO2;.    1140   0035   0012
PPMCO2AQ←44010.0×MCO2AQ;WRITE(<"NO.28">);IF FLAG3=2THEN GO TO ENDOFEH;DU.    1150   0035   0019
M←R×T/(2.0×F);IF ALFA[7]=0.0THEN FOR I←0,1,2,7,9DO EHTC[I]←-99.9ELSE BEG.    1160   0035   0027
IN EHTC[0]←EOT[0]+DUM×LN(ALFA[7]);EHTC[1]←EOT[1]-DUM×(8.0×PH×C+3.0×LN(AL.    1170   0035   0054
FA[7]));WRITE(<"NO.29">);EHTC[2]←EOT[2]-2.0×DUM×(3.0×PH×C+LN(ALFA[7]));W.    1180   0035   0060
RITE(<"NO.30">);EHTC[7]←IF MI[13]=0.0THEN-99.9ELSE EOT[7]-DUM×(4.0×PH×C+.    1190   0035   0071
LN(ALFA[7])+2.0×LN(MI[13]));WRITE(<"NO.31">);EHTC[9]←EOT[9]-DUM×(6.0×PH×.    1200   0035   0078
C+2.0×LN(ALFA[7]));WRITE(<"NO.32">);END;IF ALFA[9]=0.0THEN FOR I←4,5,6,1.    1210   0035   0087
3DO EHTC[I]←-99.9ELSE BEGIN EHTC[4]←EOT[4]-DUM×(4.0×PH×C+LN(ALFA[9]));WR.    1220   0035   0102
ITE(<"NO.33">);EHTC[5]←EOT[5]-DUM×(8.0×PH×C+3.0×LN(ALFA[9]));WRITE(<"NO..    1230   0035   0119
34">);EHTC[6]←EOT[6]-DUM×(6×PH×C+2×LN(ALFA[9]));EHTC[13]←EOT[13]-2.0×DUM.    1240   0044   0129
×(3.0×PH×C+LN(ALFA[9]));END;EHTC[3]←IF MI[13]≤0.0THEN-99.9ELSE EOT[3]-(D.    1250   0035   0137
UM/4.0)×(10.0×PH×C+LN(MI[13])-LN(ALFA[5]));WRITE(<"NO.35">);EHTC[8]←IF A.    1260   0035   0144
LFA[11]≤0.0THEN-99.9ELSE EOT[8]+DUM×LN(ALFA[11]);WRITE(<"NO.36">);EHTC[1.    1270   0035   0153
0]←IF ALFA[7]≤0OR ALFA[5]≤0THEN-99.9ELSE EOT[10]+DUM×(LN(ALFA[7])+2×LN(A.    1280   0035   0161
LFA[5])-16×PH×C)/7;DUM←1.0/DUM;FOR I←0,1,4,5,6,7,8,9DO IF EHTC[I]=-99.9T.    1290   0035   0168
HEN DELMUEH[I]←-99.9ELSE DELMUEH[I]←46.1206×(EHTC[I]-EHM);FOR I←2,13DO D.    1300   0035   0193
ELMUEH[I]←IF EHTC[I]=-99.9THEN-99.9ELSE 23.0603×(EHTC[I]-EHM);DELMUEH[3].    1310   0035   0212
←IF EHTC[3]=-99.9THEN-99.9ELSE 184.4824×(EHTC[3]-EHM);DELMUEH[10]←IF EHT.    1320   0035   0220
C[10]=-99.9THEN-99.9ELSE 322.8442×(EHTC[10]-EHM);EHTC[11]←EHTC[12]←EHM;I.    1330   0035   0225
F FLAG2=2THEN BEGIN IUP 13DO MCATEQ[I]←CREH[I]←0.0;GO TO NEXTCOMP END;CR.    1340   0035   0232
EH[0]←IF EHTC[0]=-99.9THEN 0.0ELSE EXP(DUM×(EHTC[0]-EHM));WRITE(<"NO.37".    1350   0035   0244
>);CREH[1]←IF EHTC[1]=-99.9THEN 0.0ELSE EXP(DUM×(EHM-EHTC[1])/3);WRITE(<.    1360   0047   0251
"NO.38">);CREH[2]←IF EHTC[2]=-99.9THEN 0.0ELSE EXP(DUM×(EHM-EHTC[2])/2.0.    1370   0035   0259
);WRITE(<"NO.39">);CREH[3]←IF EHTC[3]=-99.9THEN 0.0ELSE EXP(4.0×DUM×(EHT.    1380   0035   0266
C[3]-EHM));WRITE(<"NO.40">);CREH[4]←IF EHTC[4]=-99.9THEN 0.0ELSE EXP(DUM.    1390   0035   0275
×(EHM-EHTC[4]));WRITE(<"NO.41">);CREH[5]←IF EHTC[5]=-99.9THEN 0.0ELSE EX.    1400   0035   0283
P(DUM×(EHM-EHTC[5])/3.0);WRITE(<"NO.42">);CREH[6]←IF EHTC[6]=-99.9THEN 0.    1410   0035   0291
.0ELSE EXP(DUM×(EHM-EHTC[6])/2.0);WRITE(<"NO.43">);CREH[7]←IF EHTC[7]=-9.    1420   0035   0299
9.9THEN 0.0ELSE EXP(DUM×(EHM-EHTC[7]));WRITE(<"NO.44">);CREH[8]←IF EHTC[.    1430   0035   0307
8]=-99.9THEN 0.0ELSE EXP(DUM×(EHTC[8]-EHM));WRITE(<"NO.45">);CREH[9]←IF .    1440   0035   0315
EHTC[9]=-99.9THEN 0.0ELSE EXP(DUM×(EHM-EHTC[9])/2.0);WRITE(<"NO.46">);IF.    1450   0035   0324
 EHTC[10]=-99.9THEN CREH[10]←0.0ELSE BEGIN POW←7×DUM×(EHTC[10]-EHM);CREH.    1460   0035   0332
[10]←EXP(POW);CREH[13]←IF EHTC[13]=-99.9THEN 0.0ELSE EXP((DUM/2.0)×(EHM-.    1470   0035   0342
EHTC[13]));END;IF FLAG2=0THEN IUP 13DO MCATEQ[I]←0.0ELSE BEGIN MCATEQ[0].    1480   0035   0348
←EXP(DUM×(EHM-EOT[0]))/GAMMA[7];WRITE(<"NO.47">);POW←(DUM×(EOT[1]-EHM)/3.    1490   0035   0360
.0-8×PH×C/3.0);MCATEQ[1]←EXP(POW)/GAMMA[7];WRITE(<"NO.48">);POW←(DUM×(EO.    1500   0035   0368
T[2]-EHM)/2-3×PH×C);MCATEQ[2]←EXP(POW)/GAMMA[7];MCATEQ[3]←0.0;WRITE(<"NO.    1510   0035   0377
.49">);IF MI[13]≤0THEN LOGMSO4←0.0ELSE BEGIN POW←(4×DUM×(EHM-EOT[3])+10×.    1520   0059   0386
PH×C+LN(MI[13]));LOGMSO4←POW×E;END;POW←(DUM×(EOT[4]-EHM)-4×PH×C);MCATEQ[.    1530   0035   0394
4]←EXP(POW)/GAMMA[9];WRITE(<"NO.51">);POW←(DUM×(EOT[5]-EHM)/3-8×PH×C/3.0.    1540   0035   0402
);MCATEQ[5]←EXP(POW)/GAMMA[9];WRITE(<"NO.52">);POW←(DUM×(EOT[6]-EHM)/2-3.    1550   0035   0410
×PH×C);MCATEQ[6]←EXP(POW)/GAMMA[9];WRITE(<"NO.53">);IF MI[13]≤0.0THEN MC.    1560   0035   0419
ATEQ[7]←0.0ELSE BEGIN POW←(DUM×(EOT[7]-EHM)-4×PH×C-2×LN(MI[13]));MCATEQ[.    1570   0035   0428
7]←EXP(POW)/GAMMA[7];WRITE(<"NO.54">);END;POW←(DUM×(EHM-EOT[8]));MCATEQ[.    1580   0035   0437
8]←EXP(POW)/GAMMA[11];WRITE(<"NO.55">);MCATEQ[9]←10*(-3×PH)×EXP(DUM×(EOT.    1590   0035   0444
[9]-EHM)/2)/GAMMA[7];WRITE(<"NO.56">);POW←7×DUM×(EHM-EOT[10])-2×LN(ALFA[.    1600   0035   0454
5])+16×PH×C;LOGACTFEPYSO4←POW×E;MCATEQ[10]←0.0;POW←(DUM×(EOT[13]-EHM)/2-.    1610   0035   0463
3×PH×C);MCATEQ[13]←EXP(POW)/GAMMA[9];NEXTCOMP:FOR I←4,5,6,13DO PPMCATEQ[.    1620   0035   0470
I]←MCATEQ[I]×GFW[9]×10*3;FOR I←0,1,2,7,9DO PPMCATEQ[I]←MCATEQ[I]×GFW[7]×.    1630   0035   0485
10*3;PPMCATEQ[3]←MCATEQ[3]×GFW[5]×10*3;PPMCATEQ[8]←MCATEQ[8]×GFW[11]×10*.    1640   0035   0502
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3;PPMCATEQ[10]←0.0;END;ENDOFEH:DUM←2.0×F/(R×T);BEGIN LABEL DUMMY;IF FLAG.         1650    0035    0511
2=1AND MI[13]≠0AND ALFA[7]≠0THEN EOFE3S4←EHM+(8×PH×C+4×LN(MI[13])+3×LN(A.         1660    0066    0000
LFA[7]))/DUM ELSE EOFE3S4←-99.999;WRITE(<"NO.57">);IUP 11,16,17,18DO LOG.         1670    0066    0007
EKT[I]←LOGEKTO[I]-OH[I]×(1/T-1/298.16)/R;LOGEKT[12]←(C×12.0898-8.2555×LN.         1680    0066    0025
(T));IUP 12,16,17,18DO DELMU[I]←IF AP[I]=0.0THEN 99.99999ELSE R×T×(LOGEA.         1690    0066    0034
P[I]-LOGEKT[I]);IUP 12,16,17,18DO KT[I]←EXP(LOGEKT[I]);WRITE(<"NO.58">);.         1700    0066    0051
IUP 10,12,16,17,18DO APKRAT[I]←IF AP[I]=0THEN 0.0ELSE EXP(LOGEAP[I]-LOGE.         1710    0066    0073
KT[I]);WRITE(<"NO.59">);APKRAT[11]←EXP(LOGEAP[11]+17×C);WRITE(<"NO.60">).         1720    0066    0090
;FOR I←1,2,5,7,8,9,10,11,12,16,17,18DO CR[I]←APKRAT[I];FOR I←0,4,6DO CR[.         1730    0070    0100
I]←IF APKRAT[I]=0.0THEN 0.0ELSE APKRAT[I]*(1/2);CR[3]←IF APKRAT[3]=0.0TH.         1740    0066    0138
EN 0.0ELSE APKRAT[3]*(1/3);IUP 12,16,17,18DO LOGK[I]←E×LOGEKT[I];LOGME[0.         1750    0066    0146
]←0.5×LOGK[0]-PH-LOGGAMMA[11];LOGME[1]←LOGK[1]-2.0×PH-LOGGAMMA[11];LOGME.         1760    0066    0165
[2]←LOGK[2]-2.0×PH-LOGGAMMA[11];LOGME[3]←(LOGK[3]-2×PH-2×LOGALFACO3)/3-L.         1770    0066    0171
OGGAMMA[11];LOGME[4]←(LOGK[4]-2×PH-LOGALFACO3)/2-LOGGAMMA[11];IF MI[13]≤.         1780    0066    0178
0THEN FOR I←5,6DO LOGME[I]←0.0ELSE BEGIN LOGME[5]←LOGK[5]-2×PH-LOGMI13-L.         1790    0066    0184
OGGAMMA[11];LOGME[6]←(LOGK[6]-2×PH-LOGMI13)/2-LOGGAMMA[10];END;LOGME[7]←.         1800    0066    0198
LOGK[7]-LOGALFACO3-LOGGAMMA[9];LOGME[9]←LOGK[9]-LOGALFACO3-LOGGAMMA[7];L.         1810    0066    0203
OGME[8]←LOGK[8]-2×PH-LOGGAMMA[7];LOGME[10]←LOGK[10]-LOGALFACO3-LOGGAMMA[.         1820    0066    0209
1];LOGME[11]←LOGK[11]-E×LN(ALFA[1])-2×LOGALFACO3-LOGGAMMA[0];LOGME[12]←L.         1830    0066    0213
OGK[12]-LOGALFACO3-LOGGAMMA[0];LOGME[16]←LOGK[16]-2.0×PH-LOGGAMMA[9];IF .         1840    0066    0220
ALFA[5]≤0.0THEN LOGME[17]←LOGME[18]←0.0ELSE BEGIN LOGME[17]←LOGK[17]-E×L.         1850    0066    0226
N(ALFA[5])-LOGGAMMA[0];LOGME[18]←LOGK[18]-E×LN(ALFA[5])-LOGGAMMA[0];END;.         1860    0066    0233
IUP 12,16DO ME[I]←10*LOGME[I];WRITE(<"NO.61">);IF ALFA[5]≤0.0THEN ME[17].         1870    0066    0240
←ME[18]←0.0ELSE BEGIN ME[17]←10*LOGME[17];ME[18]←10*LOGME[18]END;IF MI[1.         1880    0066    0255
3]≤0.0THEN ME[5]←ME[6]←0.0;PPM[10]←MI[10]×GFW[10]×1000;PPM[11]←MI[11]×GF.         1890    0066    0265
W[11]×1000;PPM[14]←MI[14]×GFW[14]×1000.0;FOR I←1,2,3,4,5DO PPMEQ[I]←ME[I.         1900    0066    0272
]×GFW[11]×1000.0;FOR I←0,6DO PPMEQ[I]←ME[I]×GFW[10]×1000.0;FOR I←7,16DO .         1910    0066    0289
PPMEQ[I]←ME[I]×GFW[9]×1000.0;FOR I←11,12,17,18DO PPMEQ[I]←ME[I]×GFW[0]×1.         1920    0066    0308
000.0;FOR I←8,9DO PPMEQ[I]←ME[I]×GFW[7]×1000.0;PPMEQ[10]←ME[10]×GFW[1]×1.         1930    0066    0324
000.0;WRITE(PRINFIL[PAGE]);WRITE(PRINFIL,HEADF,IUP 12DO ID[I]);WRITE(PRI.         1940    0066    0338
NFIL,FORM1,PH,EHM,TEMP,MU,PCO2,MCO2AQ,PPMCO2AQ,EOFE3S4,LOGMSO4,LOGACTFEP.         1950    0066    0356
YSO4);IUP 14DO WRITE(PRINFIL,FORM2,I,PAGE1[I],PPM[I],GAMMA[I],MI[I],ALFA.         1960    0066    0371
[I]);FOR I←15,16DO WRITE(PRINFIL,FORM2,I,PAGE1[I],PPM[I]);WRITE(PRINFIL[.         1970    0066    0391
PAGE]);WRITE(PRINFIL,HEADF,IUP 12DO ID[I]);WRITE(PRINFIL,FORM3);IUP 12DO.         1980    0066    0413
 WRITE(PRINFIL,FORM4,I,PAGE2[I],AP[I],KT[I],APKRAT[I],CR[I],ME[I],PPMEQ[.         1990    0066    0434
I],DELMU[I]);FOR I←13,14,15DO WRITE(PRINFIL,FORM4,I,PAGE2[I],AP[I]);FOR .         2000    0066    0450
I←16,17,18DO WRITE(PRINFIL,FORM4,I,PAGE2[I],AP[I],KT[I],APKRAT[I],CR[I],.         2010    0066    0473
ME[I],PPMEQ[I],DELMU[I]);IF FLAG3≠1THEN GO TO START;WRITE(PRINFIL[PAGE]).         2020    0066    0492
;WRITE(PRINFIL,HEADF,IUP 12DO ID[I]);WRITE(PRINFIL,FORM5);IUP 10DO WRITE.         2030    0066    0506
(PRINFIL,FORM6,I,PAGE3[I],EOT[I],EHTC[I],CREH[I],MCATEQ[I],PPMCATEQ[I],D.         2040    0066    0526
ELMUEH[I]);FOR I←11,12DO WRITE(PRINFIL,FORM6,I,PAGE3[I]);FOR I←13DO WRIT.         2050    0066    0540
E(PRINFIL,FORM6,I,PAGE3[I],EOT[I],EHTC[I],CREH[I],MCATEQ[I],PPMCATEQ[I],.         2060    0066    0563
DELMUEH[I]);GO TO START;END;END;EOF:END.                                 .         2070    0066    0577

     EXP      IS SEGMENT 072, PRT 136         LN      IS SEGMENT 073, PRT 135         SQRT    IS SEGMENT 074, PRT 138
     WRITE    IS SEGMENT 075, PRT 129         BLK CTR IS SEGMENT 076, PRT 005         READ    IS SEGMENT 077, PRT 128
     XTOTHEI IS SEGMENT 078, PRT 137          GOTOS   IS SEGMENT 079, PRT 127         FILEOUT IS SEGMENT 080, PRT 012
     FILE IN IS SEGMENT 081, PRT 013          SELECT  IS SEGMENT 082, PRT 014
   PRT SIZE=0236;  NO. SEGS.=083;  TOTAL SEGMENT SIZE=02524;  DISK STORAGE REQ.=02524;  EST. CORE REQ.=07213.
NO ERRORS DETECTED.  ELAPSED COMPILATION TIME = 040 SECONDS.
```

Printout from test case on page D47—Continued

```
SHADMAN 40 FIELD EH PH BY CLARKE MAR 64 TEST CASE AT 74.54 DG C
NO.1
NO.10
NO.11
NO.12
NO.13
NO.14
NO.15
NO.16
NO.17
NO.18
NO.19
NO.20
NO.21
NO.22
NO.23
NO.24
NO.25
NO.26
NO.27
NO.28
NO.29
NO.30
NO.31
NO.32
NO.35
NO.36
NO.37
NO.38
NO.39
NO.40
NO.41
NO.42
NO.43
NO.44
NO.45
NO.46
NO.47
NO.48
NO.49
NO.51
NO.52
NO.53
NO.54
NO.55
NO.56
NO.57
NO.58
NO.59
NO.60
NO.61
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SHADMAN WELL 40, WEST PAKISTAN, TEST CASE AT 74.54 DG C[1]

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                         INTRINSIC THERMODYNAMIC PROPERTIES OF WATER

                                  General Characteristics

PH    EH MEAS    T     ION STRENGTH    PCO2 ATM    MCO2 AQ    PPM CO2 AQ   EO FE3S4   LOGACTSO4 EQ   LOG ACT FE PY SO4

7.55   0.0465  74.54     0.02645      0.0164487   0.000231      10.18        0.703       40.3922            62.1199

                                       Ionic Data

                 ION           PPM          GAMMA        MOLALITY      ALPHA
            0    CA          36.600       0.536246     9.1317@-04    4.8969@-04
            1    MG          24.800       0.562206     1.0201@-03    5.7349@-04
            2    NA          56.100       0.843898     2.4402@-03    2.0593@-03
            3    K            0.000       0.837220     0.0000@+00    0.0000@+00
            4    CL          12.600       0.837220     3.5540@-04    2.9755@-04
            5    SO4        912.000       0.507178     9.4939@-03    4.8151@-03
            6    HCO3       266.000       0.843898     4.3594@-03    3.6789@-03
            7    FE 2         0.500       0.536246     8.9530@-06    4.8010@-06
            8    FE 3         0.000       0.286965     0.0000@+00    0.0000@+00
            9    MN 2         0.000       0.536246     0.0000@+00    0.0000@+00
           10    CU 1         0.000       0.837220     0.0000@+00    0.0000@+00
           11    CU 2         0.000       0.536246     0.0000@+00    0.0000@+00
           12    HS           0.179       0.840629     5.4218@-06    4.5577@-06
           13    H2S          0.015       1.000000     4.4680@-07    4.4680@-07
           14    CU2OH2       0.000       0.585506     0.0000@+00    0.0000@+00
           15    CUTOT        0.000
           16    H2STOT       0.200


  THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLID PHASES UNDERGOING HYDROLYSIS REACTIONS

     PHASE        AP           KT          AP/K          CR        MOL CAT EQ    PPMCATEQUIL     DEL MU
  0  CU2O     0.0000@+00   8.6518@-03   0.0000@+00   0.0000@+00   4.8887@-09    3.1063@-04    99.99999
  1  CUO      0.0000@+00   1.7205@+06   0.0000@+00   0.0000@+00   2.5486@-09    1.6194@-04    99.99999
  2  CU(OH2   0.0000@+00   4.1621@+07   0.0000@+00   0.0000@+00   6.1652@-09    3.9174@-03    99.99999
  3  AZURIT   0.0000@+00   1.0836@-18   0.0000@+00   0.0000@+00   3.8539@-08    2.5588@-03    99.99999
  4  MALACH   0.0000@+00   1.6113@-06   0.0000@+00   0.0000@+00   2.1230@-08    1.3490@-03    99.99999
  5  CUS      0.0000@+00   4.6601@-14   0.0000@+00   0.0000@+00   1.5450@-22    9.8168@-18    99.99999
  6  CU2S     0.0000@+00   4.8904@-25   0.0000@+00   0.0000@+00   3.5219@-17    2.2378@-12    99.99999
  7  MNCO3    0.0000@+00   1.1342@-11   0.0000@+00   0.0000@+00   2.1419@-06    1.1767@-01    99.99999
  8  FE(OH2   6.0441@+09   9.9286@+10   6.0876@-02   6.0876@-02   1.4707@-04    8.2134@+00    -1.93390
  9  FECO3    4.7410@-11   7.1885@-12   6.5953@+00   6.5953@+00   1.3575@-06    7.5812@-02     1.30337
 10  MGCO3    5.6632@-09   2.8751@-09   1.9697@+00   1.9697@+00   5.1787@-04    1.2590@+01     0.46840
 11  DOLOMI   2.7385@-17   1.0000@-17   2.7385@+00   2.7385@+00   3.3345@-04    1.3365@+01     0.69608
 12  CACO3    4.8357@-09   1.2909@-09   3.7460@+00   3.7460@+00   2.4377@-04    9.7703@+00     0.91253
 13  FES      2.7005@+03
 14  CUFES2   0.0000@+00
 15  BORNIT   0.0000@+00
 16  MN(OH2   0.0000@+00   7.8462@+12   0.0000@+00   0.0000@+00   1.1622@-02    6.3851@+02    99.99999
 17  ANHYDR   2.3579@-06   1.3403@-05   1.7592@-01   1.7592@-01   5.1908@-03    2.0805@+02    -1.20067
 18  GYPSUM   2.3579@-06   2.3028@-05   1.0239@-01   1.0239@-01   8.9183@-03    3.5744@+02    -1.57462


 THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLIDS UNDERGOING OXIDATION-REDUCTION REACTIONS

     PHASE      EOT      EH T CALC         CR       MOLCATEQUIL  PPM CATEQUIL    DEL MU
  0  FE MET   -0.4375     -0.6209      4.4870@-20   1.9953@+14   1.1143@+19   -30.782008
  1  FE3O4     0.8981     -0.6350      3.8508@+06   2.3250@-12   1.2984@-07   -31.432083
  2  FE(OH3    1.0238     -0.1719      1.4647@+03   6.1126@-09   3.4137@-04    -5.036579
  3  H2S       0.2945     -0.3218      1.9518@-43   0.0000@+00   0.0000@+00   -67.949305
  4  MNO2      1.1964    -99.9000      0.0000@+00   2.5344@+03   1.3923@+08   -99.900000
  5  MN3O4     1.7563    -99.9000      0.0000@+00   4.5640@-04   2.5074@+01   -99.900000
  6  MN2O3     1.3970    -99.9000      0.0000@+00   1.5691@-03   8.6201@+01   -99.900000
  7  PY H2S   -0.1535     -0.5738      9.5639@+17   9.3613@-24   5.2280@-19   -28.606504
  8  CU MET    0.3375    -99.9000      0.0000@+00   6.8132@-09   4.3291@-04   -99.900000
  9  FE2O3     0.6671     -0.5286      2.1699@+08   4.1261@-14   2.3043@-09   -26.525900
 10  PY SO4    0.3585     -0.2858      0.0000@+00   0.0000@+00   0.0000@+00  -107.292127
 11  CUDIST
 12  CUDIST
 13  MN(OH3    2.5315    -99.9000      0.0000@+00   4.3669@+13   2.3991@+18   -99.900000
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[1] Test case at 74.54 DG C. Field Eh, pH, Fe_2, HCO_3, by Clarke, USAID and West Pakistani (WASID) Scientists, March 1964; other chemical data by USGS Laboratories.

APPENDIX 2

COMPUTER ANALYSIS, GROUND-WATER DATA, EGYPT, NIGERIA, AND WEST PAKISTAN

The amount of information generated by the data analysis is too great to embody in the text. The extracted information summarized in the section on "Results" does not provide enough of a description to compare the ground waters reported in the text to other ground waters. The data that are reported here in "Appendix 2" (p. D50–D58) give a complete description of some of the waters sampled. For complete data, see Barnes and Clarke (1967).

With few exceptions the differences that may be especially noteworthy between the waters reported here and more generally available reports on ground-water properties is that the data here reported are reasonably complete and certain particularly pertinent data represent water under field conditions.

The results of the data analysis are reported in three groups of information, all groups headed by a line of identification of the sample. The column headings are all capital letters, but correspond as closely as possible to notation used in the text. The PH and EH represent the results of field measurements of pH and platinum electrode potential reading (*Eh*) respectively. The temperature is in degrees centigrade. The ionic strength is on the molal scale and provides a quick test for the reliability of the activity coefficients. The computed P_{CO_2} in atmospheres, the molality, and parts per million of $CO_{2(aq)}$ are given.

Some calculations may not be made because of insufficient data. In such cases dummy printout is substituted. For example, if no $H_2S_{(aq)}$ or iron data are available, then no E° for the Fe_3S_4 reaction can be calculated. To avoid confusion, the E° for the Fe_3S_4 reaction is assigned a value of −99.999 if it cannot be calculated. Similarly, the $\log_{10}\alpha_{SO_4^{-2}}$ (molal scale) in equilibrium with the $H_2S_{(aq)}$ at the pH and *Eh* measured cannot be calculated if $H_2S_{(aq)}$ data are not available. In such a case an impossible value of 0.0000 is assigned. The entire $\log_{10}\alpha_{Fe^{+2}}$ (molal) in equilibrium with pyrite at the *Eh* and pH measured at the activity of SO_4^{-2} found is also given, and clearly shows that pyrite is not in equilibrium with the solutions studied.

The description of the sample composition lists the identity (0, 1, and so forth) of the species in the computations. The chemical identity of the species (ION) is also given. The concentration of the species in parts per million (PPM), the activity coefficients (GAMMA), the concentration in molal units (MOLALITY) and the activity of the species in molality (ALPHA) are given.

The mass-action reactions are identified (0, 1, and so forth) in the same array sequence as in the program and the text of the paper, and identified by the name of the appropriate solid. The computed activity products (*AP*), and equilibrium constants at the field temperature (*KT*) and their ratios give a quick test for the relation of the actual properties of the solutions to the equilibrium properties. The ratio of the metal cation as it actually is in solution to the metal cation at equilibrium with the appropriate solid (all other properties held constant) and the concentrations (both parts per million and molality) of the metal cation at equilibrium with the solid are given for the convenience of the readers more accustomed to compositional variables. The $\Delta\mu_R$ (DEL MU) values in kcal give the direction of the departures from equilibrium by their signs and give the extent, by the magnitude of the $\Delta\mu_R$ values. Where insufficient data are available to compute the various parameters, standard dummy values are inserted. They are as follows:

Heading	*Dummy value if computation cannot be made*
AP	0.0000 @+00
AP/K	0.0000 @+00
CR	0.0000 @+00
MOL CAT EQ	0.0000 @+00
PPMCATEQUIL	0.0000 @+00
DEL MU	99.99999

Oxidation reactions are listed in the same numerical sequence as in the program and text. The identification of the solid under consideration is also given. The oxidation of $H_2S_{(aq)}$ to SO_4^{-2} is identified as H_2S, and the copper ion oxidation reactions used in the distribution of copper species are identified as CUDIST. The standard oxidation potential at the temperature of the solution in the field (EOT) is given along with the Eh calculation from the solution properties and compositions under the field conditions. The ratio of the actual metal cation to the metal cation at equilibrium with the appropriate solid and the concentration of the metal cation at equilibrium with the solid both in molality (MOL CATEQUIL) and parts per million (PPM) are given for the convenience of readers more accustomed to concentrations as operational variables. The values of $\Delta\mu_R$ (DEL MU) give the direction of the departures from equilibrium by their signs and give the extent, by the magnitude of the $\Delta\mu_R$ values. Because necessary data may be missing, some variables cannot be computed in some cases. Dummy values are substituted and are chosen to be readily noticed and then disregarded. The dummy values are:

Heading	*Dummy values*
EH T CALC	−99.9000
CR	0.0000 @+00
MOL CATEQUIL	0.0000 @+00
PPM CATEQUIL	0.0000 @+00
DEL MU	−99.900000

KEY TO COMPUTER PROGRAM COLUMN HEADINGS

Column headings	*Definition*
ALPHA	Activity molal scale.
AP	Activity product.
AP/K	Activity product/equilibrium constant.
CR	Cation, actual/cation at equilibrium.
DEL MU	Actual chemical potential.
EH MEAS	Oxidation-reduction potential, volt.
EH T CALC	Calculated oxidation-reduction potential at observed temperature.
EO FE3S4	Standard potential, Fe_3S_4.
EOT	Standard state potential at observed temperature.
GAMMA	Activity coefficient.
ION	Ion.
ION STRENGTH	Ionic strength.
KT	Equilibrium constant at observed temperature.
LOG ACT FE PY SO4	Log activity of iron in equilibrium with pyrite at the measured SO_4, *Eh*, and pH.

Column headings	*Definition*
LOGACTSO4 EQ	Log activity of SO_4 at equilibrium with H_2S at the measured pH and *Eh*.
MCO2 AQ	Molality aqueous CO_2.
MOLALITY	Molality.
MOL CAT EQ MOL CATEQUIL	Molality of cation at equilibrium.
PCO2 ATM	Partial pressure of CO_2 in atmospheres.
PH	pH.
PHASE	Solid phase.
PPM	Concentrations in parts per million.
PPMCATEQUIL	Parts per million of cation at equilibrium.
PPM CO2 AQ	Aqueous CO_2, ppm.
T	Temperature, degrees centigrade.

KHARGA WELL 1, EGYPT[1]

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                              INTRINSIC THERMODYNAMIC PROPERTIES OF WATER

                                        General Characteristics

 PH   EH MEAS    T    ION STRENGTH  PCO2 ATM  MCO2 AQ   PPM CO2 AQ  EO FE3S4  LOGACTSO4 EQ  LOG ACT FE PY SO4

6.91  -0.0034  38.00    0.00361    0.0156605 0.000392     17.23      0.729      25.0952          35.1668

                                              Ionic Data

                    ION         PPM          GAMMA       MOLALITY      ALPHA
                 0  CA        14.000       0.773233    3.4930@-04  2.7009@-04
                 1  MG         4.900       0.780074    2.0155@-04  1.5722@-04
                 2  NA        22.000       0.935515    9.5695@-04  8.9524@-04
                 3  K         27.000       0.934348    6.9050@-04  6.4517@-04
                 4  CL        34.000       0.934348    9.5902@-04  8.9606@-04
                 5  SO4       12.000       0.765956    1.2492@-04  9.5683@-05
                 6  HCO3     104.000       0.935515    1.7044@-03  1.5945@-03
                 7  FE 2       2.600       0.773233    4.6556@-05  3.5998@-05
                 8  FE 3       0.000       0.577287    0.0000@+00  0.0000@+00
                 9  MN 2       0.273       0.773233    4.9775@-06  3.8487@-06
                10  CU 1       0.000       0.934348    0.0000@+00  0.0000@+00
                11  CU 2       0.000       0.773233    0.0000@+00  0.0000@+00
                12  HS         1.224       0.934937    3.7007@-05  3.4600@-05
                13  H2S        0.939       1.000000    2.7547@-05  2.7547@-05
                14  CU2OH2     0.000       0.786517    0.0000@+00  0.0000@+00
                15  CUTOT      0.000
                16  H2STOT     2.200


     THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLID PHASES UNDERGOING HYDROLYSIS REACTIONS

        PHASE        AP           KT          AP/K          CR        MOL CAT EQ    PPMCATEQUIL     DEL MU
     0  CU2O     0.0000@+00  1.6163@-02  0.0000@+00  0.0000@+00  2.0228@-08   1.2853@-03    99.99999
     1  CUO      0.0000@+00  2.5345@+07  0.0000@+00  0.0000@+00  4.9611@-07   3.1523@-02    99.99999
     2  CU(OH2   0.0000@+00  5.4590@+08  0.0000@+00  0.0000@+00  1.0686@-05   6.7897@-01    99.99999
     3  AZURIT   0.0000@+00  1.0836@-18  0.0000@+00  0.0000@+00  3.9475@-07   2.5083@-02    99.99999
     4  MALACH   0.0000@+00  1.6113@-06  0.0000@+00  0.0000@+00  2.3176@-07   1.4726@-02    99.99999
     5  CUS      0.0000@+00  2.3445@-15  0.0000@+00  0.0000@+00  1.6660@-24   1.0586@-19    99.99999
     6  CU2S     0.0000@+00  1.4133@-27  0.0000@+00  0.0000@+00  9.4312@-19   5.9926@-14    99.99999
     7  MNCO3    2.9229@-12  1.3512@-11  2.1631@-91  2.1631@-01  2.3010@-05   1.2641@+00    -0.94669
     8  FE(OH2   2.3784@+09  4.0597@+12  5.8586@-04  5.8586@-04  7.9466@-02   4.4379@+03    -4.60191
     9  FECO3    2.7338@-11  1.5790@-11  1.7313@+00  1.7313@+00  2.6890@-05   1.5017@+00     0.33940
    10  MGCO3    1.1940@-10  8.0256@-09  1.4877@-02  1.4877@-02  1.3547@-02   3.2936@+02    -2.60190
    11  DOLOMI   2.4491@-20  1.0000@-17  2.4491@-03  2.4491@-03  1.4263@-01   5.7164@+03    -3.71745
    12  CACO3    2.0512@-10  3.2283@-09  6.3537@-02  6.3537@-02  5.4976@-03   2.2034@+02    -1.70421
    13  FES      6.5517@+04
    14  CUFES2   0.0000@+00
    15  BORNIT   0.0000@+00
    16  MN(OH2   2.5428@+08  4.0014@+14  6.3548@-07  6.3548@-07  7.8326@+00   4.3031@+05    -8.82294
    17  ANHYDR   2.5843@-08  2.7600@-05  9.3636@-04  9.3636@-04  3.7304@-01   1.4951@+04    -4.31196
    18  GYPSUM   2.5843@-08  2.4003@-05  1.0767@-03  1.0767@-03  3.2442@-01   1.3003@+04    -4.22562


    THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLIDS UNDERGOING OXIDATION-REDUCTION REACTIONS

        PHASE      EOT      EH T CALC          CR       MOL CATEQUIL PPM CATEQUIL    DEL MU
     0  FE MET   -0.4393    -0.5765       2.7226@-19   1.7100@+14   9.5496@+18  -26.432246
     1  FE3O4     0.9595    -0.3355       3.8519@+03   1.2087@-08   6.7500@-04  -15.315482
     2  FE(OH3    1.0481     0.0426       1.7977@-01   2.5898@-04   1.4463@+01    1.061123
     3  H2S       0.3010    -0.2281       7.6854@-30   0.0000@+00   0.0000@+00  -41.452017
     4  MNO2      1.2204     0.5343       3.8195@-18   1.3032@+12   7.1593@+16   24.799154
     5  MN3O4     1.8036     0.5986       3.1624@-07   1.5740@+01   8.6470@+05   27.763398
     6  MN2O3     1.4312     0.4856       1.1996@-08   4.1492@+02   2.2795@+07   22.555188
     7  PY H2S   -0.1436    -0.5782       4.1509@+18   1.1216@-23   6.2637@-19  -26.507891
     8  CU MET    0.3371   -99.9000       0.0000@+00   1.2031@-11   7.6447@-07  -99.900000
     9  FE2O3     0.7119    -0.2936       5.0163@+04   9.2809@-10   5.1831@-05  -13.384497
    10  PY SO4    0.3645    -0.1781       2.4517@-40   0.0000@+00   0.0000@+00  -56.396163
    11  CUDIST
    12  CUDIST
    13  MN(OH3    2.0547     1.1091       9.5627@-19   5.2051@+12   2.8596@+17   25.655448
```

[1] Field Eh, pH, HCO_3, by Clarke, USAID, and Egyptian Scientists (EGDDO), June 1962; S Data by EGDDO; other chemical data by USGS Laboratories, July 1965.

NASSER WELL 1, EGYPT[1]

INTRINSIC THERMODYNAMIC PROPERTIES OF WATER

General Characteristics

PH	EH MEAS	T	ION STRENGTH	PCO2 ATM	MCO2 AQ	PPM CO2 AQ	EO FE3S4	LOGACTSO4 EQ	LOG ACT FE PY SO4
6.70	-0.0210	31.00	0.01012	0.0188927	0.000554	24.37	0.660	19.6137	23.7373

Ionic Data

	ION	PPM	GAMMA	MOLALITY	ALPHA
0	CA	34.000	0.672359	8.4830@-04	5.7036@-04
1	MG	28.000	0.686476	1.1517@-03	7.9061@-04
2	NA	36.000	0.900286	1.5659@-03	1.4098@-03
3	K	38.000	0.897442	9.7182@-04	8.7215@-04
4	CL	116.000	0.897442	3.2719@-03	2.9364@-03
5	SO4	111.000	0.656934	1.1555@-03	7.5909@-04
6	HCO3	89.500	0.900286	1.4668@-03	1.3205@-03
7	FE 2	4.200	0.672359	7.5205@-05	5.0565@-05
8	FE 3	0.000	0.438311	0.00C0@+00	0.0000@+00
9	MN 2	0.414	0.672359	7.5378@-06	5.0681@-06
10	CU 1	0.000	0.897442	0.0000@+00	0.0000@+00
11	CU 2	0.000	0.672359	0.0000@+00	0.0000@+00
12	HS	0.685	0.898884	2.0719@-05	1.8624@-05
13	H2S	0.994	1.000000	2.9164@-05	2.9164@-05
14	CU2OH2	0.000	0.699442	0.0000@+00	0.0000@+00
15	CUTOT	0.000			
16	H2STOT	1.700			

THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLID PHASES UNDERGOING HYDROLYSIS REACTIONS

	PHASE	AP	KT	AP/K	CR	MOL CAT EQ	PPMCATEQUIL	DEL MU
0	CU2O	0.0000@+00	1.8533@-02	0.0000@+00	0.0000@+00	4.0399@-08	2.5670@-03	99.99999
1	CUO	0.0000@+00	4.5679@+07	0.0000@+00	0.0000@+00	2.7047@-06	1.7186@-01	99.99999
2	CU(OH2	0.0000@+00	9.5920@+08	0.0000@+00	0.0000@+00	5.6795@-05	3.6087@+00	99.99999
3	AZURIT	0.0000@+00	1.0836@-18	0.0000@+00	0.0000@+00	1.0561@-06	6.7106@-02	99.99999
4	MALACH	0.0000@+00	1.6113@-06	0.0000@+00	0.0000@+00	6.3937@-07	4.0626@-02	99.99999
5	CUS	0.0000@+00	1.2182@-15	0.0000@+00	0.0000@+00	2.4733@-24	1.5715@-19	99.99999
6	CU2S	0.0000@+00	3.9280@-28	0.0000@+00	0.0000@+00	8.1594@-19	5.1845@-14	99.99999
7	MNCO3	1.7592@-12	1.4040@-11	1.2530@-01	1.2530@-01	6.0159@-05	3.3050@+00	-1.25543
8	FE(OH2	1.2701@+09	9.1501@+12	1.3881@-04	1.3881@-04	5.4178@-01	3.0257@+04	-5.36873
9	FECO3	1.7552@-11	1.8760@-11	9.3560@-01	9.3560@-01	8.0382@-05	4.4891@+00	-0.04023
10	MGCO3	2.7443@-10	1.0049@-08	2.7310@-02	2.7310@-02	4.2171@-02	1.0253@+03	-2.17623
11	DOLOMI	5.4332@-20	1.0000@-17	5.4332@-03	5.4332@-03	1.5613@-01	6.2578@+03	-3.15220
12	CACO3	1.9798@-10	3.8954@-09	5.0824@-02	5.0824@-02	1.6691@-02	6.6897@+02	-1.80081
13	FES	3.7042@+04						
14	CUFES2	0.0000@+00						
15	BORNIT	0.0000@+00						
16	MN(OH2	1.2731@+08	9.4659@+14	1.3449@-07	1.3449@-07	5.6048@+01	3.0792@+06	-9.56306
17	ANHYDR	4.3296@-07	3.2330@-05	1.3392@-02	1.3392@-02	6.3344@-02	2.5388@+03	-2.60694
18	GYPSUM	4.3296@-07	2.4222@-05	1.7875@-02	1.7875@-02	4.7458@-02	1.9021@+03	-2.43242

THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLIDS UNDERGOING OXIDATION-REDUCTION REACTIONS

	PHASE	EOT	EH T CALC	CR	MOL CATEQUIL	PPM CATEQUIL	DEL MU
0	FEMET	-0.4397	-0.5693	6.7435@-19	1.1152@+14	6.2282@+18	-25.289416
1	FE3O4	0.9713	-0.2572	4.0701@+02	1.8478@-07	1.0319@-02	-10.895652
2	FE(OH3	1.0528	0.0990	1.0266@-02	7.3255@-03	4.0911@+02	2.767593
3	H2S	0.3023	-0.1925	1.8474@-23	0.0000@+00	0.0000@+00	-31.638969
4	MNO2	1.2250	0.5761	1.6339@-20	4.6135@+14	2.5346@+19	27.538000
5	MN3O4	1.8127	0.6746	2.0699@-08	3.6417@+02	2.0007@+07	32.082550
6	MN2O3	1.4378	0.5443	4.3008@-10	1.7527@+04	9.6288@+08	26.071275
7	PY H2S	-0.1417	-0.5471	2.7130@+17	2.7720@-22	1.5481@-17	-24.262778
8	CU MET	0.3371	-99.9000	0.0000@+00	2.0252@-12	1.2868@-07	-99.900000
9	FE2O3	0.7205	-0.2333	3.2908@+03	2.2853@-08	1.2763@-03	-9.790332
10	PY SO4	0.3657	-0.1418	9.2589@-29	0.0000@+00	0.0000@+00	-39.015180
11	CUDIST						
12	CUDIST						
13	MN(OH3	1.9634	1.0699	8.4108@-19	8.9621@+12	4.9236@+17	25.155874

[1] Field Eh, pH, HCO_3, by Clarke, USAID, and Egyptian Scientists (EGDDO), June 1962; S Data by EGDDO; other chemical data by USGS Laboratories, July 1965.

NASSER WELL 3, EGYPT[1]

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                         INTRINSIC THERMODYNAMIC PROPERTIES OF WATER

                                   General Characteristics

PH    EH MEAS    T    ION STRENGTH   PCO2 ATM  MCO2 AQ  PPM CO2 AQ  EO FE3S4  LOGACTSO4 EQ  LOG ACT FE PY SO4

6.89  -0.0282  37.00    0.00420     0.0169914 0.000434    19.11       0.641      21.1493          28.9905

                                       Ionic Data

                 ION         PPM         GAMMA        MOLALITY      ALPHA
             0   CA         18.000      0.759944     4.4910@-04   3.4129@-04
             1   MG         11.000      0.767601     4.5245@-04   3.4730@-04
             2   NA          0.000      0.931153     0.0000@+00   0.0000@+00
             3   K          27.000      0.929819     6.9050@-04   6.4204@-04
             4   CL         59.000      0.929819     1.6642@-03   1.5474@-03
             5   SO4        11.000      0.751769     1.1451@-04   8.6085@-05
             6   HCO3      110.000      0.931153     1.8028@-03   1.6787@-03
             7   FE 2        2.100      0.759944     3.7603@-05   2.8576@-05
             8   FE 3        0.000      0.557429     0.0000@+00   0.0000@+00
             9   MN 2        0.282      0.759944     5.1356@-06   3.9028@-06
            10   CU 1        0.050      0.929819     7.8651@-07   7.3131@-07
            11   CU 2        0.000      0.759944     1.0562@-09   8.0267@-10
            12   HS          0.486      0.930493     1.4703@-05   1.3681@-05
            13   H2S         0.399      1.000000     1.1705@-05   1.1705@-05
            14   CU2OH2      0.000      0.774787     2.6890@-15   2.0834@-15
            15   CUTOT       0.050
            16   H2STOT      0.900


  THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLID PHASES UNDERGOING HYDROLYSIS REACTIONS

       PHASE        AP          KT          AP/K         CR        MOL CAT EQ     PPMCATEQUIL     DEL MU
   0   CU2O     3.2226@+01  1.6475@-02  1.9560@+03  4.4227@+01   2.1759@-08     1.3826@-03     4.67108
   1   CUO      4.8366@+04  2.7525@+07  1.7572@-03  1.7572@-03   6.0110@-07     3.8194@-02    -3.91013
   2   CU(OH2   4.8366@+04  5.9076@+08  8.1871@-05  8.1871@-05   1.2901@-05     8.1974@-01    -5.80005
   3   AZURIT   1.7648@-26  1.0836@-18  1.6286@-08  2.5348@-03   4.1670@-07     2.6477@-02   -11.05294
   4   MALACH   2.9216@-11  1.6113@-06  1.8132@-05  4.2581@-03   2.4805@-07     1.5761@-02    -6.72918
   5   CUS      5.6613@-01  2.1390@-15  2.6467@+14  2.6467@+14   3.9908@-24     2.5358@-19    20.46856
   6   CU2S     3.7721@-04  1.1812@-27  3.1934@+23  5.6510@+11   1.3918@-18     8.8435@-14    33.35703
   7   MNCO3    2.9370@-12  1.3585@-11  2.1620@-01  2.1620@-01   2.3754@-05     1.3050@+00    -0.94397
   8   FE(OH2   1.7219@+09  4.5492@+12  3.7850@-04  3.7850@-04   9.9347@-02     5.5482@+03    -4.85638
   9   FECO3    2.1505@-11  1.6176@-11  1.3294@+00  1.3294@+00   2.8285@-05     1.5796@+00     0.17550
  10   MGCO3    2.6136@-10  8.2824@-09  3.1556@-02  3.1556@-02   1.4338@-02     3.4858@+02    -2.13008
  11   DOLOMI   6.7128@-20  1.0000@-17  6.7128@-03  6.7128@-03   6.6902@-02     2.6814@+03    -3.08403
  12   CACO3    2.5684@-10  3.3152@-09  7.7473@-02  7.7473@-02   5.7969@-03     2.3234@+02    -1.57651
  13   FES      2.0155@+04
  14   CUFES2   1.1410@+04
  15   BORNIT   1.6235@-03
  16   MN(OH2   2.3517@+08  4.5144@+14  5.2092@-07  5.2092@-07   9.8588@+00     5.4162@+05    -8.91710
  17   ANHYDR   2.9380@-08  2.8218@-05  1.0412@-03  1.0412@-03   4.3134@-01     1.7288@+04    -4.23270
  18   GYPSUM   2.9380@-08  2.4033@-05  1.2225@-03  1.2225@-03   3.6737@-01     1.4724@+04    -4.13376

 THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLIDS UNDERGOING OXIDATION-REDUCTION REACTIONS

       PHASE      EOT      EH T CALC          CR      MOL CATEQUIL PPM CATEQUIL    DEL MU
   0   FE MET   -0.4394    -0.5792       1.2401@-18   3.0323@+13   1.6934@+18   -25.412814
   1   FE3O4     0.9612    -0.3155       1.2932@+03   2.9076@-08   1.6238@-03   -13.248214
   2   FE(OH3    1.0488     0.0564       4.2239@-02   8.9024@-04   4.9717@+01     1.950375
   3   H2S       0.3012    -0.2222       6.1037@-26   0.0000@+00   0.0000@+00   -35.784061
   4   MNO2      1.2211     0.5394       3.5720@-19   1.4377@+13   7.8987@+17    26.179943
   5   MN3O4     1.8049     0.6081       1.2798@-07   4.0128@+01   2.2045@+06    29.346808
   6   MN2O3     1.4322     0.4929       3.4040@-09   1.5087@+03   8.2885@+07    24.035443
   7   PY H2S   -0.1433    -0.5481       7.8401@+16   4.7962@-22   2.6785@-17   -23.976272
   8   CU MET    0.3371     0.0573       5.9850@+02   1.7648@-12   1.1213@-07     3.941190
   9   FE2O3     0.7132    -0.2793       1.2018@+04   3.1289@-09   1.7474@-04   -11.580104
  10   PY SO4    0.3647    -0.1756       2.9208@-34   0.0000@+00   0.0000@+00   -47.591868
  11   CUDIST
  12   CUDIST
  13   MN(OH3    2.0417     1.1024       4.2484@-19   1.2088@+13   6.6411@+17    26.073059
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[1] Field Eh, pH, HCO_3, by Clarke, USAID, and Egyptian Scientists (EGDDO), June 1962; S Data by EGDDO; other chemical data by USGS Laboratories, July 1965.

DALORI WELL, NIGERIA[1/]

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                               INTRINSIC THERMODYNAMIC PROPERTIES OF WATER

                                          General Characteristics

 PH   EH MEAS     T     ION STRENGTH   PCO2 ATM    MCO2 AQ    PPM CO2 AQ   EO FE3S4   LOGACTSO4 EQ   LOG ACT FE PY SO4

7.29  -0.2671   31.00     0.00567     0.0104106   0.000305      13.44      -99.999      0.0000             -22.8288

                                               Ionic Data

                        ION           PPM         GAMMA        MOLALITY        ALPHA
                   0    CA          14.000      0.733457     3.4930@-04     2.5620@-04
                   1    MG           6.800      0.742919     2.7970@-04     2.0779@-04
                   2    NA          76.000      0.922203     3.3058@-03     3.0486@-03
                   3    K           14.000      0.920482     3.5804@-04     3.2957@-04
                   4    CL          10.000      0.920482     2.8206@-04     2.5963@-04
                   5    SO4         29.000      0.723279     3.0189@-04     2.1835@-04
                   6    HCO3       187.500      0.922203     3.0729@-03     2.8338@-03
                   7    FE 2         7.000      0.733457     1.2534@-04     9.1933@-05
                   8    FE 3         0.000      0.519398     0.0000@+00     0.0000@+00
                   9    MN 2         1.024      0.733457     1.8631@-05     1.3665@-05
                  10    CU 1         0.040      0.920482     6.2952@-07     5.7947@-07
                  11    CU 2         0.000      0.733457     8.4928@-14     6.2291@-14
                  12    HS           0.000      0.921352     0.0000@+00     0.0000@+00
                  13    H2S          0.000      1.000000     0.0000@+00     0.0000@+00
                  14    CU2OH2       0.000      0.751737     6.2143@-23     4.6715@-23
                  15    CUTOT        0.040
                  16    H2STOT       0.000

          THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLID PHASES UNDERGOING REACTIONS

            PHASE        AP           KT          AP/K          CR        MOL CAT EQ   PPMCATEQUIL    DEL MU
        0   CU2O    1.2766@+02   1.8533@-02   6.8882@+03   8.2995@+01   9.5192@-09   6.0485@-04    5.34164
        1   CUO     2.3682@+01   4.5679@+07   5.1845@-07   5.1845@-07   1.6381@-07   1.0409@-02   -8.74747
        2   CU(OH2  2.3682@+01   9.5920@+08   2.4690@-08   2.4690@-08   3.4398@-06   2.1857@-01  -10.58762
        3   AZURIT  7.7173@-37   1.0836@-18   7.1217@-19   8.9302@-07   9.5102@-08   6.0428@-03  -25.25643
        4   MALACH  4.2751@-18   1.6113@-06   2.6532@-12   1.6289@-06   5.2139@-08   3.3129@-03  -16.11107
        5   CUS     0.0000@+00   1.2182@-15   0.0000@+00   0.0000@+00   0.0000@+00   0.0000@+00   99.99999
        6   CU2S    0.0000@+00   3.9280@-28   0.0000@+00   0.0000@+00   0.0000@+00   0.0000@+00   99.99999
        7   MNCO3   3.9600@-11   1.4040@-11   2.8205@+00   2.8205@+00   6.6055@-06   3.6289@-01    0.62673
        8   FE(OH2  3.4952@+10   9.1501@+12   3.8199@-03   3.8199@-03   3.2813@-02   1.8325@+03   -3.36515
        9   FECO3   2.6642@-10   1.8760@-11   1.4202@+01   1.4202@+01   8.8259@-06   4.9290@-01    1.60375
       10   MGCO3   6.0218@-10   1.0049@-08   5.9926@-02   5.9926@-02   4.6674@-03   1.1347@+02   -1.70124
       11   DOLOMI  4.4709@-19   1.0000@-17   4.4709@-02   4.4709@-02   7.8128@-03   3.1314@+02   -1.87829
       12   CACO3   7.4245@-10   3.8954@-09   1.9060@-01   1.9060@-01   1.8327@-03   7.3453@+01   -1.00188
       13   FES     0.0000@+00
       14   CUFES2  0.0000@+00
       15   BORNIT  0.0000@+00
       16   MN(OH2  5.1952@+09   9.4659@+14   5.4883@-06   5.4883@-06   3.3946@+00   1.8649@+05   -7.32132
       17   ANHYDR  5.5941@-08   3.2330@-05   1.7303@-03   1.7303@-03   2.0187@-01   8.0910@+03   -3.84380
       18   GYPSUM  5.5941@-08   2.4222@-05   2.3095@-03   2.3095@-03   1.5124@-01   6.0618@+03   -3.66928

     THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLIDS UNDERGOING OXIDATION-REDUCTION REACTIONS

                         EOT       EH T CALC          CR       MOL CATEQUIL PPM CATEQUIL   DEL MU
        0   FE MET   -0.4397     -0.5615        1.7538@-10   7.1469@+05   3.9913@+10 -13.577810
        1   FE3O4     0.9713     -0.4232        5.2975@+01   2.3661@-06   1.3214@-01  -7.198348
        2   FE(OH3    1.0528     -0.0235        9.1896@-05   1.3640@+00   7.6173@+04   5.618032
        3   H2S       0.3023    -99.9000        0.0000@+00   0.0000@+00   0.0000@+00 -99.900000
        4   MNO2      1.2250      0.4919        7.0549@-26   2.6408@+20   1.4508@+25  35.004286
        5   MN3O4     1.8127      0.4932        3.9952@-09   4.6632@+03   2.5619@+08  35.065348
        6   MN2O3     1.4378      0.4115        5.7090@-12   3.2633@+06   1.7928@+11  31.295818
        7   PY H2S   -0.1417    -99.9000        0.0000@+00   0.0000@+00   0.0000@-00 -99.900000
        8   CU MET    0.3371     -0.0614        6.5438@+06   1.2978@-20   8.2465@-16   9.485839
        9   FE2O3     0.7205     -0.3558        2.9457@+01   4.2551@-06   2.3763@-01  -4.089453
       10   PY SO4    0.3657     -0.1861        6.1978@+18   0.0000@+00   0.0000@+00  26.153855
       11   CUDIST
       12   CUDIST
       13   MN(OH3    1.9634      0.9371        1.1165@-20   1.6687@+15   9.1674@+19  27.768145
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[1/] Field Eh, pH, Fe_2, HCO_3, by Clarke, USAID, and Nigerian Scientists, Feb. 1965; remaining determinations by USGS Laboratories, May 1965.

NGALA, NIGERIA[1]

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                         INTRINSIC THERMODYNAMIC PROPERTIES OF WATER

                                  General Characteristics

PH    EH MEAS    T     ION STRENGTH  PCO2 ATM    MCO2 AQ    PPM CO2 AQ  EO FE3S4  LOGACTSO4 EQ  LOG ACT FE PY SO4

6.70  0.0274   40.00    0.00987     0.0874851  0.002094     92.14     -99.999     0.0000          37.8085

                                        Ionic Data

                 ION        PPM        GAMMA        MOLALITY      ALPHA
              0  CA         8.000     0.671086     1.9960@-04   1.3395@-04
              1  MG         4.100     0.685152     1.6864@-04   1.1554@-04
              2  NA       176.000     0.899872     7.6556@-03   6.8890@-03
              3  K          9.000     0.897039     2.3017@-04   2.0647@-04
              4  CL        34.000     0.897039     9.5902@-04   8.6028@-04
              5  SO4       83.000     0.655728     8.6403@-04   5.6657@-04
              6  HCO3     360.000     0.899872     5.9000@-03   5.3092@-03
              7  FE 2       0.300     0.671086     5.3718@-06   3.6050@-06
              8  FE 3       0.000     0.436400     0.0000@+00   0.0000@+00
              9  MN 2       0.416     0.671086     7.5747@-06   5.0832@-06
             10  CU 1       0.000     0.897039     0.0000@+00   0.0000@+00
             11  CU 2       0.000     0.671086     0.0000@+00   0.0000@+00
             12  HS         0.000     0.898476     0.0000@+00   0.0000@+00
             13  H2S        0.000     1.000000     0.0000@+00   0.0000@+00
             14  CU2OH2     0.000     0.698079     0.0000@+00   0.0000@+00
             15  CUTOT      0.000
             16  H2STOT     0.000

   THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLID PHASES UNDERGOING HYDROLYSIS REACTIONS

         PHASE        AP          KT         AP/K         CR       MOL CAT EQ    PPMCATEQUIL     DEL MU
     0   CU2O     0.0000@+00  1.5560@-02  0.0000@+00  0.0000@+00  3.7088@-08    2.3566@-03    99.99999
     1   CUO      0.0000@+00  2.1522@+07  0.0000@+00  0.0000@+00  1.2768@-06    8.1126@-02    99.99999
     2   CU(OH2   0.0000@+00  4.6686@+08  0.0000@+00  0.0000@+00  2.7695@-05    1.7598@+00    99.99999
     3   AZURIT   0.0000@+00  1.0836@-18  0.0000@+00  0.0000@+00  3.8159@-07    2.4246@-02    99.99999
     4   MALACH   0.0000@+00  1.6113@-06  0.0000@+00  0.0000@+00  2.9811@-07    1.8942@-02    99.99999
     5   CUS      0.0000@+00  2.8116@-15  0.0000@+00  0.0000@+00  0.0000@+00    0.0000@+00    99.99999
     6   CU2S     0.0000@+00  2.0162@-27  0.0000@+00  0.0000@+00  0.0000@+00    0.0000@+00    99.99999
     7   MNCO3    8.1474@-12  1.3369@-11  6.0942@-01  6.0942@-01  1.2429@-05    6.8284@-01    -0.30820
     8   FE(OH2   9.0552@+07  3.2401@+12  2.7948@-05  2.7948@-05  1.9221@-01    1.0734@+04    -6.52501
     9   FECO3    5.7780@-12  1.5053@-11  3.8385@-01  3.8385@-01  1.3995@-05    7.8156@-01    -0.59587
    10   MGCO3    1.8520@-10  7.5402@-09  2.4561@-02  2.4561@-02  6.8662@-03    1.6693@+02    -2.30664
    11   DOLOMI   3.9760@-20  1.0000@-17  3.9760@-03  3.9760@-03  5.0201@-02    2.0120@+03    -3.43979
    12   CACO3    2.1469@-10  3.0620@-09  7.0116@-02  7.0116@-02  2.8467@-03    1.1410@+02    -1.65385
    13   FES      0.0000@+00
    14   CUFES2   0.0000@+00
    15   BORNIT   0.0000@+00
    16   MN(OH2   1.2769@+08  3.1510@+14  4.0522@-07  4.0522@-07  1.8693@+01    1.0269@+06    -9.15965
    17   ANHYDR   7.5891@-08  2.6414@-05  2.8731@-03  2.8731@-03  6.9472@-02    2.7844@+03    -3.64197
    18   GYPSUM   7.5891@-08  2.3942@-05  3.1698@-03  3.1698@-03  6.2970@-02    2.5238@+03    -3.58082

  THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLIDS UNDERGOING OXIDATION-REDUCTION REACTIONS

         PHASE      EOT      EH T CALC         CR       MOL CATEQUIL PPM CATEQUIL     DEL MU
     0   FE MET   -0.4392    -0.6083      3.4495@-21   1.5573@+15   8.6969@+19   -29.320721
     1   FE3O4     0.9561    -0.2018      2.8787@+02   1.8661@-08   1.0421@-03   -10.571474
     2   FE(OH3    1.0468     0.1361      1.7832@-02   3.0124@-04   1.6823@+01     2.505873
     3   H2S       0.3007   -99.9000      0.0000@+00   0.0000@+00   0.0000@+00   -99.900000
     4   MNO2      1.2191     0.5509      1.4117@-17   5.3657@+11   2.9478@+16    24.145042
     5   MN3O4     1.8010     0.6292      3.4969@-07   2.1661@+01   1.1900@+06    27.754121
     6   MN2O3     1.4294     0.5093      1.7542@-08   4.3180@+02   2.3722@+07    22.227182
     7   PY H2S   -0.1441   -99.9000      0.0000@+00   0.0000@+00   0.0000@+00   -99.900000
     8   CU MET    0.3372   -99.9000      0.0000@+00   1.5956@-10   1.0138@-05   -99.900000
     9   FE2O3     0.7095    -0.2013      4.7882@+03   1.1219@-09   6.2654@-05   -10.546777
    10   PY SO4    0.3642    -0.1646      5.6022@-44   0.0000@+00   0.0000@+00   -61.976060
    11   CUDIST
    12   CUDIST
    13   MN(OH3    2.0808     1.1608      5.7539@-19   1.3164@+13   7.2322@+17    26.136479
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[1] Field Eh, pH, Fe_2, HCO_3, by Clarke, USAID, and Nigerian Scientists, Feb. 1965; remaining determinations by USGS Laboratories, May 1965.

SHADMAN WELL 27, WEST PAKISTAN[1]

INTRINSIC THERMODYNAMIC PROPERTIES OF WATER

General Characteristics

PH	EH MEAS	T	ION STRENGTH	PCO2 ATM	MCO2 AQ	PPM CO2 AQ	EO FE3S4	LOGACTSO4 EQ	LOG ACT FE PY SO4
7.69	0.0580	28.00	0.00693	0.0054415	0.000172	7.57	0.759	38.7765	58.5980

Ionic Data

	ION	PPM	GAMMA	MOLALITY	ALPHA
0	CA	42.000	0.714253	1.0479@-03	7.4847@-04
1	MG	16.000	0.725125	6.5811@-04	4.7721@-04
2	NA	35.000	0.915505	1.5224@-03	1.3938@-03
3	K	5.000	0.913464	1.2787@-04	1.1681@-04
4	CL	13.000	0.913464	3.6668@-04	3.3495@-04
5	SO4	18.000	0.702496	1.8738@-04	1.3163@-04
6	HCO3	259.100	0.915505	4.2463@-03	3.8875@-03
7	FE 2	0.220	0.714253	3.9393@-06	2.8137@-06
8	FE 3	0.000	0.492974	0.0000@+00	0.0000@+00
9	MN 2	0.099	0.714253	1.8068@-06	1.2905@-06
10	CU 1	0.000	0.913464	0.0000@+00	0.0000@+00
11	CU 2	0.000	0.714253	0.0000@+00	0.0000@+00
12	HS	0.920	0.914497	2.7812@-05	2.5434@-05
13	H2S	0.152	1.000000	4.4655@-06	4.4655@-06
14	CU2OH2	0.000	0.735208	0.0000@+00	0.0000@+00
15	CUTOT	0.000			
16	H2STOT	1.100			

THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLID PHASES UNDERGOING HYDROLYSIS REACTIONS

	PHASE	AP	KT	AP/K	CR	MOL CAT EQ	PPMCATEQUIL	DEL MU
0	CU2O	0.0000@+00	1.9691@-02	0.0000@+00	0.0000@+00	4.0113@-09	2.5488@-04	99.99999
1	CUO	0.0000@+00	5.9293@+07	0.0000@+00	0.0000@+00	3.4606@-08	2.1988@-03	99.99999
2	CU(OH2	0.0000@+00	1.2311@+09	0.0000@+00	0.0000@+00	7.1854@-07	4.5656@-02	99.99999
3	AZURIT	0.0000@+00	1.0836@-18	0.0000@+00	0.0000@+00	2.4023@-08	1.5265@-03	99.99999
4	MALACH	0.0000@+00	1.6113@-06	0.0000@+00	0.0000@+00	1.1800@-08	7.4977@-04	99.99999
5	CUS	0.0000@+00	9.1162@-16	0.0000@+00	0.0000@+00	1.1915@-25	7.5708@-21	99.99999
6	CU2S	0.0000@+00	2.2282@-28	0.0000@+00	0.0000@+00	1.5789@-19	1.0032@-14	99.99999
7	MNCO3	1.2203@-11	1.4281@-11	8.5451@-01	8.5451@-01	2.1144@-06	1.1616@-01	-0.09409
8	FE(OH2	6.7495@+09	1.3113@+13	5.1472@-04	5.1472@-04	7.6533@-03	4.2742@+02	-4.53149
9	FECO3	2.6606@-11	2.0247@-11	1.3141@+00	1.3141@+00	2.9978@-06	1.6742@-01	0.16345
10	MGCO3	4.5126@-09	1.1100@-08	4.0652@-01	4.0652@-01	1.6189@-03	3.9359@+01	-0.53869
11	DOLOMI	3.1938@-17	1.0000@-17	3.1938@+00	3.1938@+00	3.2811@-04	1.3151@+01	0.69494
12	CACO3	7.0776@-09	4.2276@-09	1.6741@+00	1.6741@+00	6.2593@-04	2.5087@+01	0.30839
13	FES	3.0140@+04						
14	CUFES2	0.0000@+00						
15	BORNIT	0.0000@+00						
16	MN(OH2	3.0957@+09	1.3859@+15	2.2336@-06	2.2336@-06	8.0890@-01	4.4439@+04	-7.78712
17	ANHYDR	9.8523@-08	3.4675@-05	2.8413@-03	2.8413@-03	3.6881@-01	1.4782@+04	-3.50908
18	GYPSUM	9.8523@-08	2.4319@-05	4.0513@-03	4.0513@-03	2.5866@-01	1.0367@+04	-3.29677

THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLIDS UNDERGOING OXIDATION-REDUCTION REACTIONS

	PHASE	EOT	EH T CALC	CR	MOL CATEQUIL	PPM CATEQUIL	DEL MU
0	FE MET	-0.4398	-0.6057	6.1218@-23	6.4349@+16	3.5937@+21	-30.609901
1	FE3O4	0.9763	-0.3643	5.1399@+04	7.6643@-11	4.2803@-06	-19.475216
2	FE(OH3	1.0548	0.0079	6.8893@+00	5.7181@-07	3.1934@-02	-1.155013
3	H2S	0.3028	-0.2606	2.2023@-43	0.0000@+00	0.0000@+00	-58.781938
4	MNO2	1.2270	0.4839	5.5686@-15	3.2446@+08	1.7825@+13	19.642506
5	MN3O4	1.8166	0.5063	9.9561@-06	1.8147@-01	9.9698@+03	20.678052
6	MN2O3	1.4406	0.4139	1.1058@-06	1.6339@+00	8.9764@+04	16.415746
7	PY H2S	-0.1409	-0.5744	1.4639@+21	2.6910@-27	1.5029@-22	-29.166275
8	CU MET	0.3370	-99.9000	0.0000@+00	6.4148@-10	4.0760@-05	-99.900000
9	FE2O3	0.7242	-0.3227	2.3482@+06	1.6776@-12	9.3689@-08	-17.557876
10	PY SO4	0.3662	-0.2158	0.0000@+00	0.0000@+00	0.0000@+00	-88.397619
11	CUDIST						
12	CUDIST						
13	MN(OH3	1.9242	0.8976	8.9197@-15	2.0256@+08	1.1128@+13	19.360559

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[1] Field Eh, pH, Fe_2, HCO_3, S, by Clarke, USAID, and W. Pakistani (WASID) Scientists, March 1965; other chemical data by USGS Laboratories, May 1965.

SHADMAN WELL 47, WEST PAKISTAN[1]

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                         INTRINSIC THERMODYNAMIC PROPERTIES OF WATER

                                   General Characteristics

 PH   EH MEAS    T    ION STRENGTH  PCO2 ATM  MCO2 AQ   PPM CO2 AQ  EO FE3S4  LOGACTSO4 EQ  LOG ACT FE PY SO4

7.50  0.0815   27.00   0.01033     0.0115304 0.000373    16.44      0.738      39.9759         59.8760

                                       Ionic Data

                 ION         PPM          GAMMA       MOLALITY     ALPHA
             0   CA         53.000       0.671814    1.3224@-03   8.8838@-04
             1   MG         18.000       0.686045    7.4038@-04   5.0793@-04
             2   NA         77.000       0.900053    3.3493@-03   3.0146@-03
             3   K           3.400       0.897182    8.6952@-05   7.8012@-05
             4   CL         22.000       0.897182    6.2054@-04   5.5674@-04
             5   SO4        56.000       0.656256    5.8296@-04   3.8257@-04
             6   HCO3      365.500       0.900053    5.9901@-03   5.3914@-03
             7   FE 2        0.200       0.671814    3.5812@-06   2.4059@-06
             8   FE 3        0.000       0.437770    0.0000@+00   0.0000@+00
             9   MN 2        0.169       0.671814    3.0748@-06   2.0657@-06
            10   CU 1        0.148       0.897182    2.3255@-06   2.0864@-06
            11   CU 2        0.012       0.671814    1.9454@-07   1.3069@-07
            12   HS          0.697       0.898638    2.1089@-05   1.8952@-05
            13   H2S         0.181       1.000000    5.3193@-06   5.3193@-06
            14   CU2OH2      0.000       0.699108    5.1083@-10   3.5713@-10
            15   CUTOT       0.160
            16   H2STOT      0.900


   THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLID PHASES UNDERGOING HYDROLYSIS REACTIONS

        PHASE        AP          KT          AP/K         CR       MOL CAT EQ    PPMCATEQUIL     DEL MU
    0   CU2O     4.3529@+03  2.0098@-02  2.1658@+05  4.6538@+02  6.6731@-09   4.2401@-04     7.32813
    1   CUO      1.3069@+08  6.4754@+07  2.0183@+00  2.0183@+00  9.6386@-08   6.1244@-03     0.41889
    2   CU(OH2   1.3069@+08  1.3394@+09  9.7576@-02  9.7576@-02  1.9937@-06   1.2668@-01    -1.38807
    3   AZURIT   1.5403@-16  1.0836@-18  1.4215@+02  5.2189@+00  3.7276@-08   2.3685@-03     2.95664
    4   MALACH   1.4189@-04  1.6113@-06  8.8057@+01  9.3838@+00  2.0731@-08   1.3173@-03     2.67100
    5   CUS      6.9521@+02  8.2659@-16  8.4106@+17  8.4106@+17  2.3130@-25   1.4697@-20    24.61857
    6   CU2S     2.3155@-02  1.8399@-28  1.2585@+26  1.1218@+13  2.0729@-19   1.3171@-14    35.84644
    7   MNCO3    1.7159@-11  1.4383@-11  1.1947@+00  1.1947@+00  2.5738@-06   1.4140@-01     0.10610
    8   FE(OH2   2.4059@+09  1.4808@+13  1.6248@-04  1.6248@-04  2.2041@-02   1.2309@+03    -5.20423
    9   FECO3    1.9985@-11  2.0776@-11  9.6191@-01  9.6191@-01  3.7230@-06   2.0792@-01    -0.02316
   10   MGCO3    4.2191@-09  1.1480@-08  3.6752@-01  3.6752@-01  2.0145@-03   4.8977@+01    -0.59706
   11   DOLOMI   3.1134@-17  1.0000@-17  3.1134@+00  3.1134@+00  4.2472@-04   1.7023@+01     0.67744
   12   CACO3    7.3793@-09  4.3452@-09  1.6983@+00  1.6983@+00  7.7865@-04   3.1208@+01     0.31589
   13   FES      1.2798@+04
   14   CUFES2   8.8972@+06
   15   BORNIT   4.7701@+03
   16   MN(OH2   2.0657@+09  1.5764@+15  1.3104@-06  1.3104@-06  2.3465@+00   1.2891@+05    -8.07938
   17   ANHYDR   3.3987@-07  3.5505@-05  9.5722@-03  9.5722@-03  1.3814@-01   5.5368@+03    -2.77295
   18   GYPSUM   3.3987@-07  2.4352@-05  1.3956@-02  1.3956@-02  9.4750@-02   3.7976@+03    -2.54804


  THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLIDS UNDERGOING OXIDATION-REDUCTION REACTIONS

        PHASE      EOT      EH T CALC       CR       MOL CATEQUIL PPM CATEQUIL   DEL MU
    0   FE MET   -0.4399    -0.6072     7.4560@-24   4.8031@+17   2.6824@+22   -31.764095
    1   FE3O4     0.9780    -0.3068     2.2202@+04   1.6130@-10   9.0081@-06   -17.908467
    2   FE(OH3    1.0555     0.0501     3.3728@+00   1.0618@-06   5.9298@-02    -0.725160
    3   H2S       0.3030    -0.2416     4.0440@-44   0.0000@+00   0.0000@+00   -59.597702
    4   MNO2      1.2277     0.5036     6.7103@-15   4.5822@+08   2.5174@+13    19.466036
    5   MN3O4     1.8179     0.5390     7.5670@-06   4.0635@-01   2.2324@+04    21.100385
    6   MN2O3     1.4415     0.4401     9.5444@-07   3.2216@+00   1.7699@+05    16.536834
    7   PY H2S   -0.1406    -0.5525     1.9574@+21   1.8296@-27   1.0218@-22   -29.242711
    8   CU MET    0.3370     0.1320     4.9753@+01   3.9101@-09   2.4845@-04     2.330471
    9   FE2O3     0.7254    -0.2800     1.1737@+06   3.0512@-12   1.7040@-07   -16.672280
   10   PY SO4    0.3664    -0.1971     0.0000@+00   0.0000@+00   0.0000@+00   -89.952712
   11   CUDIST
   12   CUDIST
   13   MN(OH3    1.9112     0.9097     1.2425@-14   2.4748@+08   1.3596@+13    19.098585
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[1] Field Eh, pH Fe_2, HCO_3, S, by Clarke, USAID, and W. Pakistani (WASID) Scientists, March 1964; other chemical data by USGS Laboratories, July 1964.

SHAHKOT WELL 251, WEST PAKISTAN[1]

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                              INTRINSIC THERMODYNAMIC PROPERTIES OF WATER

                                        General Characteristics

 PH    EH MEAS    T    ION STRENGTH   PCO2 ATM  MCO2 AQ   PPM CO2 AQ  EO FE3S4  LOGACTSO4 EQ  LOG ACT FE PY SO4

8.12   0.1185  21.00    0.00465     0.0009029  0.000034      1.52      0.832     49.7868         77.2045

                                             Ionic Data

                    ION          PPM          GAMMA        MOLALITY     ALPHA
                 0  CA          27.000       0.756080     6.7365@-04   5.0934@-04
                 1  MG          10.000       0.764134     4.1132@-04   3.1430@-04
                 2  NA          19.000       0.929816     8.2645@-04   7.6845@-04
                 3  K            4.300       0.928401     1.0997@-04   1.0210@-04
                 4  CL           6.800       0.928401     1.9180@-04   1.7807@-04
                 5  SO4         42.000       0.747461     4.3722@-04   3.2680@-04
                 6  HCO3       125.600       0.929816     2.0584@-03   1.9140@-03
                 7  FE 2         0.220       0.756080     3.9393@-06   2.9785@-06
                 8  FE 3         0.000       0.552103     0.0000@+00   0.0000@+00
                 9  MN 2         0.105       0.756080     1.9077@-06   1.4424@-06
                10  CU 1         0.000       0.928401     0.0000@+00   0.0000@+00
                11  CU 2         0.000       0.756080     0.0000@+00   0.0000@+00
                12  HS           0.451       0.929116     1.3627@-05   1.2661@-05
                13  H2S          0.036       1.000000     1.0446@-06   1.0446@-06
                14  CU2OH2       0.000       0.771677     0.0000@+00   0.0000@+00
                15  CUTOT        0.000
                16  H2STOT       0.500


     THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLID PHASES UNDERGOING HYDROLYSIS REACTIONS

         PHASE        AP           KT          AP/K          CR        MOL CAT EQ   PPMCATEQUIL    DEL MU
      0  CU2O     0.0000@+00  2.2791@-02  0.0000@+00  0.0000@+00  1.5147@-09   9.6241@-05   99.99999
      1  CUO      0.0000@+00  1.1125@+08  0.0000@+00  0.0000@+00  8.4673@-09   5.3801@-04   99.99999
      2  CU(OH2   0.0000@+00  2.2481@+09  0.0000@+00  0.0000@+00  1.7110@-07   1.0872@-02   99.99999
      3  AZURIT   0.0000@+00  1.0836@-18  0.0000@+00  0.0000@+00  1.0706@-08   6.8025@-04   99.99999
      4  MALACH   0.0000@+00  1.6113@-06  0.0000@+00  0.0000@+00  3.8676@-09   2.4575@-04   99.99999
      5  CUS      0.0000@+00  4.5296@-16  0.0000@+00  0.0000@+00  3.3002@-26   2.0970@-21   99.99999
      6  CU2S     0.0000@+00  5.6742@-29  0.0000@+00  0.0000@+00  6.0221@-20   3.8264@-15   99.99999
      7  MNCO3    1.5640@-11  1.4878@-11  1.0512@+00  1.0512@+00  1.8147@-06   9.9696@-02    0.02921
      8  FE(OH2   5.1760@+10  3.1243@+13  1.6567@-03  1.6567@-03  2.3778@-03   1.3279@+02   -3.74285
      9  FECO3    3.2296@-11  2.4340@-11  1.3269@+00  1.3269@+00  2.9689@-06   1.6580@-01    0.16533
     10  MGCO3    3.4081@-09  1.4114@-08  2.4147@-01  2.4147@-01  1.7034@-03   4.1413@+01   -0.83065
     11  DOLOMI   1.8822@-17  1.0000@-17  1.8822@+00  1.8822@+00  3.5790@-04   1.4345@+01    0.36971
     12  CACO3    5.5229@-09  5.1334@-09  1.0759@+00  1.0759@+00  6.2615@-04   2.5096@+01    0.04275
     13  FES      5.4067@+04
     14  CUFES2   0.0000@+00
     15  BORNIT   0.0000@+00
     16  MN(OH2   2.5065@+10  3.4773@+15  7.2083@-06  7.2083@-06  2.6465@-01   1.4539@+04   -6.92126
     17  ANHYDR   1.6645@-07  4.1059@-05  4.0540@-03  4.0540@-03  1.6617@-01   6.6602@+03   -3.21975
     18  GYPSUM   1.6645@-07  2.4556@-05  6.7784@-03  6.7784@-03  9.9382@-02   3.9832@+03   -2.91926


    THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLIDS UNDERGOING OXIDATION-REDUCTION REACTIONS

         PHASE      EOT      EH T CALC        CR       MOL CATEQUIL PPM CATEQUIL   DEL MU
      0  FE MET  -0.4402     -0.6015      2.1365@-25   1.8438@+19   1.0297@+24   -33.205739
      1  FE3O4    0.9881     -0.4239      1.5675@+06   2.5131@-12   1.4035@-07   -25.015882
      2  FE(OH3   1.0595     -0.0398      5.1590@+02   7.6358@-09   4.2644@-04    -3.651063
      3  H2S      0.3041     -0.2702      0.0000@+00   0.0000@+00   0.0000@+00   -71.703800
      4  MNO2     1.2316      0.4542      3.1490@-12   6.0581@+05   3.3282@+10    15.481240
      5  MN3O4    1.8256      0.4412      2.0591@-04   9.2644@-03   5.0897@+02    14.885119
      6  MN2O3    1.4472      0.3662      5.6965@-05   3.3489@-02   1.8398@+03    11.425736
      7  PY H2S  -0.1390     -0.5765      6.5251@+23   6.0372@-30   3.3716@-25   -32.053969
      8  CU MET   0.3370    -99.9000      0.0000@+00   4.3247@-08   2.7479@-03   -99.900000
      9  FE2O3    0.7328     -0.3665      2.0392@+08   1.9318@-14   1.0788@-09   -22.368750
     10  PY SO4   0.3673     -0.2264      0.0000@+00   0.0000@+00   0.0000@+00  -111.353649
     11  CUDIST
     12  CUDIST
     13  MN(OH3   1.8329      0.7520      1.4028@-11   1.3599@+05   7.4711@+09    14.607935
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[1] Field Eh, pH, Fe_2, HCO_3, S, by Clarke, USAID, and W. Pakistani (WASID) Scientists, March 1965; other chemical data by USGS Laboratories, May 1965.

SHAHKOT WELL 252, WEST PAKISTAN[1]

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                         INTRINSIC THERMODYNAMIC PROPERTIES OF WATER

                                   General Characteristics

PH   EH MEAS    T    ION STRENGTH   PCO2 ATM  MCO2 AQ   PPM CO2 AQ  EO FE3S4  LOGACTSO4 EQ  LOG ACT FE PY SO4

8.12  0.3392  22.00    0.00414     0.0008992 0.000033     1.47      -99.999      0.0000          130.5429

                                        Ionic Data

                ION        PPM          GAMMA       MOLALITY     ALPHA
            0   CA        28.000       0.766404    6.9860@-04   5.3541@-04
            1   MG         8.800       0.773797    3.6196@-04   2.8008@-04
            2   NA        15.000       0.933235    6.5246@-04   6.0890@-04
            3   K          3.800       0.931957    9.7182@-05   9.0569@-05
            4   CL         3.800       0.931957    1.0718@-04   9.9891@-05
            5   SO4       28.000       0.758515    2.9148@-04   2.2109@-04
            6   HCO3     123.000       0.933235    2.0158@-03   1.8812@-03
            7   FE 2       0.000       0.766414    0.0000@+00   0.0000@+00
            8   FE 3       0.000       0.567350    0.0000@+00   0.0000@+00
            9   MN 2       0.000       0.766414    0.0000@+00   0.0000@+00
           10   CU 1       0.000       0.931957    0.0000@+00   0.0000@+00
           11   CU 2       0.000       0.766414    0.0000@+00   0.0000@+00
           12   HS         0.000       0.932602    0.0000@+00   0.0000@+00
           13   H2S        0.000       1.000000    0.0000@+00   0.0000@+00
           14   CU2OH2     0.000       0.780738    0.0000@+00   0.0000@+00
           15   CUTOT      0.000
           16   H2STOT     0.000


   THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLID PHASES UNDERGOING HYDROLYSIS REACTIONS

       PHASE        AP          KT          AP/K         CR       MOL CAT EQ   PPMCATEQUIL    DEL MU
   0   CU2O     0.0000@+00  2.2310@-02  0.0000@+00  0.0000@+00  1.4784@-09   9.3939@-05   99.99999
   1   CUO      0.0000@+00  1.0150@+08  0.0000@+00  0.0000@+00  7.6211@-09   4.8424@-04   99.99999
   2   CU(OH2   0.0000@+00  2.0592@+09  0.0000@+00  0.0000@+00  1.5461@-07   9.8241@-03   99.99999
   3   AZURIT   0.0000@+00  1.0836@-18  0.0000@+00  0.0000@+00  1.0527@-08   6.6887@-04   99.99999
   4   MALACH   0.0000@+00  1.6113@-06  0.0000@+00  0.0000@+00  3.8061@-09   2.4184@-04   99.99999
   5   CUS      0.0000@+00  5.0157@-16  0.0000@+00  0.0000@+00  0.0000@+00   0.0000@+00   99.99999
   6   CU2S     0.0000@+00  6.9262@-29  0.0000@+00  0.0000@+00  0.0000@+00   0.0000@+00   99.99999
   7   MNCO3    0.0000@+00  1.4789@-11  0.0000@+00  0.0000@+00  1.7708@-06   9.7285@-02   99.99999
   8   FE(OH2   0.0000@+00  2.7529@+13  0.0000@+00  0.0000@+00  2.0670@-03   1.1543@+02   99.99999
   9   FECO3    0.0000@+00  2.3696@-11  0.0000@+00  0.0000@+00  2.8373@-06   1.5845@-01   99.99999
  10   MGCO3    3.0521@-09  1.3628@-08  2.2395@-01  2.2395@-01  1.6162@-03   3.9294@+01   -0.87765
  11   DOLOMI   1.7807@-17  1.0000@-17  1.7807@+00  1.7807@+00  3.9231@-04   1.5724@+01    0.33845
  12   CACO3    5.8344@-09  4.9916@-09  1.1688@+00  1.1688@+00  5.9769@-04   2.3955@+01    0.09151
  13   FES      0.0000@+00
  14   CUFES2   0.0000@+00
  15   BORNIT   0.0000@+00
  16   MN(OH2   0.0000@+00  3.0410@+15  0.0000%+00  0.0000@+00  2.2832@-01   1.2544@+04   99.99999
  17   ANHYDR   1.1838@-07  4.0060@-05  2.9549@-03  2.9549@-03  2.3642@-01   9.4757@+03   -3.41617
  18   GYPSUM   1.1838@-07  2.4522@-05  4.8274@-03  4.8274@-03  1.4472@-01   5.8003@+03   -3.12828

  THERMODYNAMIC STATE OF WATER WITH RESPECT TO COEXISTING SOLIDS UNDERGOING OXIDATION-REDUCTION REACTIONS

       PHASE      EOT     EH T CALC         CR      MOLCATEQUIL  PPMCATEQUIL    DEL MU
   0   FE MET   -0.4402   -99.9000      0.0000@+00  5.3700@+26  2.9990@+31  -99.900000
   1   FE3O4     0.9864   -99.9000      0.0000@+00  6.7498@-15  3.7696@-10  -99.900000
   2   FE(OH3    1.0588   -99.9000      0.0000@+00  1.1030@-12  6.1601@-08  -99.900000
   3   H2S       0.3039   -99.9000      0.0000@+00  0.0000@+00  0.0000@+00  -99.900000
   4   MNO2      1.2309   -99.9000      0.0000@+00  1.2246@-02  6.7275@+02  -99.900000
   5   MN3O4     1.8244   -99.9000      0.0000@+00  2.3328@-05  1.2816@+00  -99.900000
   6   MN2O3     1.4462   -99.9000      0.0000@+00  4.5448@-06  2.4968@-01  -99.900000
   7   PY H2S   -0.1393   -99.9000      0.0000@+00  0.0000@+00  0.0000@+00  -99.900000
   8   CU MET    0.3370   -99.9000      0.0000@+00  1.5553@+00  9.8822@+04  -99.900000
   9   FE2O3     0.7316   -99.9000      0.0000@+00  2.8515@-18  1.5925@-13  -99.900000
  10   PY SO4    0.3672   -99.9000      0.0000@+00  0.0000@+00  0.0000@+00  -99.900000
  11   CUDIST
  12   CUDIST
  13   MN(OH3    1.8459   -99.9000      1.4028@-11  3.0377@+01  1.6688@+06  -99.900000
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[1] Field Eh, pH, Fe_2, HCO_3, S, by Clarke, USAID, and W. Pakistani (WASID) Scientists, March 1965; other chemical data by USGS Laboratories, May 1965.

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