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Computer Code for Producing Eh–pH Plots of Equilibrium Chemical Systems†

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This paper describes a computer code that produces high-quality potential (Eh)–pH diagrams by coupling the power of the computer for handling extensive calculations with modern digital graphics hardware. The code, called EHPH, is written in standard FORTRAN 77 and has been designed to offer the user considerable flexibility as well as ease of use. The code produces three Eh vs. pH plots for each problem submitted: (1) a plot of the regions of stability for the stable solid species, (2) a plot of the regions of dominance of the dominant aqueous species, and (3) a contour plot of the total solubility of all species. The DISSPLA graphics package is employed in production of the plots.[1] A user's guide is available.[2]

INTRODUCTION

Potential–pH (Eh–pH) diagrams are useful analytical tools for understanding the thermodynamic relationships between species in chemical systems.[3,4] In engineering applications, for instance, Eh–pH analysis may be used to predict how corrosion product formation depends on the electrochemical environment. Geochemical studies use Eh–pH analysis to infer conditions under which various geologic units were formed or to determine stable mineral assemblages under given conditions. The thermodynamic basis upon which Eh–pH analysis rests is straightforward, but the calculations required to plot an Eh–pH diagram are extremely tedious and time consuming. These two qualities make Eh–pH analysis an ideal application for computers, which, in addition to making calculations rapidly, thrive on tedium.

The computer code described in this paper produces high-quality Eh–pH diagrams by coupling the speed of the computer with modern digital graphics hardward. The EHPH code is written in standard FORTRAN 77 and has been designed to offer the user considerable flexibility as well as ease of use. The code produces three plots for each problem submitted: (1) a plot of the regions of stability for the stable solid species, (2) a plot of the regions of dominance of the dominant aqueous species, and (3) a contour plot of the total solubility of all species.

The code is simple to use, requiring as input only a list of the species formed from the element under investigation, corresponding thermodynamic data, and concentrations of complexing species. The necessary thermodynamic data may exist in one of several forms, such as free energies of formation or reaction, standard electrode potentials, or equilibrium constants. The code includes modules for interactive entry of the necessary data to simplify input.

The program includes a mechanism for relating the thermodynamic data to nonstandard temperatures using entropy data. In addition, the code allows the user to include the speciation of sulfur-bearing complexing species; if this option is ignored, S(VI) is assumed throughout the Eh range.

The user has full control over the pH and Eh ranges to be covered in the analysis and subsequently plotted. Default values are included for most of the input requested from the user, and several calculation and plotting options are included. In addition to graphical output, the program also produces a log file to preserve a record of the details of the calculation.

The code was developed on a PRIME 750 computer using the PRIMOS operating system. System routines have been avoided except for a few that have analogs in virtually all systems. Thus, conversion to other FORTRAN 77 systems should be reasonably simple. A user's guide has been written

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to explain the code and its use in detail.[2]

EH–PH ANALYSIS

While a thorough explanation of Eh–pH analysis is beyond the scope of this paper, a brief introduction will be presented here to facilitate an understanding of the EHPH code. Detailed explanations of the technique are available elsewhere.[3,4]

Analysis of equilibrium solution chemistry is complex because many elements can exist in a number of oxidation states, each of which can generally form a variety of oxyions and hydroxyl complexes. The presence of other complexing species and the possibility that the solution is in equilibrium with various solid species further complicate the analysis of such systems. Thus, solution composition varies both with the pH and with the oxidation potential. Consequently, an understanding of the chemistry of an aqueous system requires a method for relating concentrations of the various species to these variables.

Eh–pH analysis of a chemical system is accomplished by identifying the solid and aqueous chemical species present in the system, choosing one, preferably aqueous, as a base-line species, and writing balanced reaction equations for each non-base-line species in terms of the base-line species. A set of algebraic equations relating the concentrations of the species can then be derived from either the Nernst equation (for oxidation–reduction reactions) or the equilibrium expression. For instance, for a general oxidation–reduction reaction

$$aA + bB \rightleftarrows cC + dD + ne^-$$

the Nernst equation becomes

$$\mathrm{Eh} = E^\circ + \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

If one of the species in the balanced reaction is the hydrogen ion, it can be removed from the log term as pH (after conversion from natural to common logs). The resulting equation thus relates the oxidized and reduced species in terms of Eh and pH (and concentrations of any complexing species involved).

A multispecies system, of course, requires a set of such equations. For a given Eh and pH, however, a thermodynamically stable solid species and a dominant aqueous species can be found from the set of equations. The analysis is conceptually simple but often requires considerable computation making it ideal as a computer application.

EHPH CODE ORGANIZATION

The various logical functions required to produce an Eh–pH diagram have been divided into separate subprogram units within the EHPH framework. The code is subdivided into three main operations, each of which requires several subroutines for completion. First, the problem is set up by opening various input and output files and then reading and interpreting the input needed for the system being investigated. This portion of the code is highly interactive, and the user is prompted by the program for the names of data files to be used and conditions to be assumed during the run. Where the data files do not exist, the program and the user create them in the correct format through another interactive procedure; these files are then saved for future use. The user needs little or no understanding of the file structure required by the program, since all input files can be created interactively.

Once the problem has been defined in the setup portion of the code, the solution is obtained. The solution consists of a matrix of total aqueous concentration values covering the Eh–pH range under consideration and a scratch file containing points that define the solid species and aqueous species stability boundaries. Finally, the graphic output is produced from routines contained in the DISSPLA graphics package.[1]

INPUT REQUIREMENTS

Considerable effort has been expended in the development of EHPH to make the program input as simple as possible. Solution of Eh–pH problems is essentially a problem of solving a system of linear equations formed by taking the logarithm of the expression for the equilibrium constants for all the reactions in the system. For example, consider the reaction

$$2Fe^{2+} + 3H_2O \rightleftarrows Fe_2O_3(s) + 6H^+ + 2e^-$$

for which the equilibrium constant is given by

$$[Fe_2O_3(s)][H^+]^6[e^-]^2/([Fe^{2+}]^2[H_2O]^3) = K$$

Taking the common log of both sides yields the more useful form

$$\log [Fe_2O_3(s)] - 6\mathrm{pH} - 2C\mathrm{Eh} - 2 \log [Fe^{2+}] - 3 \log [H_2O] = \log K$$

where $C = F/(2.303RT)$ (T is the absolute temperature, R is the gas constant, and F is the Faraday constant). The analysis, then, requires stoichiometric coefficients, equilibrium constants, and various species concentrations.

Stoichiometric coefficients are determined from the balanced reactions for the formation of the species of interest from a base-line species (in this case Fe^{2+}). The program has been designed so that only the names of the species need to be input; the program balances the reactions automatically, using the first one entered as the base-line species. This simplifies the data input considerably, while eliminating numerous sources of input error.

Equilibrium constants for the reactions in the system may be obtained from a variety of sources. For example, the equilibrium constants can be calculated from the free energies of formation for the species involved in the reaction. For other problems, a tabulation of free energies for the reactions themselves, or the corresponding equilibrium constants, may be available. Finally, it may be more convenient to specify the oxidation potential for oxidation–reduction reactions. For some systems of interest, the data base available for specifying the problem may consist of more than one of these sources. The program is designed to handle any combination of these alternative methods of specifying the thermodynamic input without requiring the user to convert from one form to another. Again, there is an obvious benefit in time saving to the user and elimination of potential data input error.

Finally, the program requires information on the concentrations of the species involved in the various reactions. For species of the element of interest, these concentrations are either assumed to be unity (in the case of solids and water) or are computed. For other complexing species involved in the reactions (carbonate, sulfate, chloride, etc.), the concentrations are calculated within the program from input specifying the total concentration of the species of interest. For example, in the analyses considered under Output, both carbonate and sulfate are involved. The input to the program specifies the total carbon and sulfur content of the water, and the code speciates them appropriately for the relevant Eh and pH conditions. For most of the complexing species, this speciation is dependent only on pH. For sulfur, however, the important Eh-dependent sulfate–sulfide speciation is also considered unless the user elects to ignore it.

OUTPUT

The user interface to EHPH has been designed to allow the user to enter as many run parameters as possible and, at the

same time, to require as few as possible. The large number of defaults included and extensive consistency checking of the entered data allow the program to be quite robust, producing either normal output or else affording an analysis of why such output cannot be produced. Normal output consists of two forms. The main output is the graphical representation of the Eh–pH relationships. As the graphical output is an expression of the problem under consideration, however, it is important that the problem can be reconstructed when analyzing the plots. Since the readability of the graphical output would be seriously impaired by including all of the conditions of the system it represents, the program has been set up to produce a log file to record the details of the problem. The two types of output are linked by a random number assigned by the program.

EXAMPLE

The iron–water system is of considerable practical importance in disciplines ranging from geochemistry to corrosion engineering. This system was submitted to EHPH as a verification of its operation and for benchmark testing, using thermodynamic data in the form of free energies of formation from Garrels and Christ.[3] The iron species included in the test were chosen to conform to the Garrels and Christ analysis rather than to the current state of knowledge of the iron–water system. The results are intended to illustrate and confirm the operation of the program rather than to reveal intricacies of the chemical system, which would require a more current data base.

The iron–water system considered here consists of the following iron species: Fe^{2+}, Fe^{3+}, $FeOH^{2+}$, $Fe(OH)_2^+$, $HFeO_2^-$, FeO_2^-, Fe(s), FeO(s), $Fe_2O_3(s)$, $Fe_3O_4(s)$, $Fe(OH)_2(s)$, $Fe(OH)_3(s)$, FeS(s), $FeS_2(s)$, $FeCO_3(s)$, and $FeSO_4(s)$. The species may be related by a set of oxidation–reduction and equilibrium reactions with their corresponding equilibrium constants:

$Fe^{2+} = Fe^{3+} + e^-$	K_1	(1)
$Fe^{2+} + H_2O = FeOH^{2+} + H^+ + e^-$	K_2	(2)
$Fe^{2+} + 2H_2O = Fe(OH)_2^+ + 2H^+ + e^-$	K_3	(3)
$Fe^{2+} + 2H_2O = HFeO_2^- + 3H^+$	K_4	(4)
$Fe^{2+} + 2H_2O = FeO_2^- + 4H^+ + e^-$	K_5	(5)
$Fe^{2+} + 2e^- = Fe(s)$	K_6	(6)
$Fe^{2+} + H_2O = FeO(s) + 2H^+$	K_7	(7)
$2Fe^{2+} + 3H_2O = Fe_2O_3(s) + 6H^+ + 2e^-$	K_8	(8)
$3Fe^{2+} + 4H_2O = Fe_3O_4(s) + 8H^+ + 2e^-$	K_9	(9)
$Fe^{2+} + 2H_2O = Fe(OH)_2(s) + 2H^+$	K_{10}	(10)
$Fe^{2+} + 3H_2O = Fe(OH)_3(s) + 3H^+ + e^-$	K_{11}	(11)
$Fe^{2+} + SO_4^{2-} + 8H^+ + 8e^- = FeS(s) + 4H_2O$	K_{12}	(12)
$Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^- = FeS_2(s) + 8H_2O$	K_{13}	(13)
$Fe^{2+} + CO_3^{2-} = FeCO_3(s)$	K_{14}	(14)
$Fe^{2+} + SO_4^{2-} = FeSO_4(s)$	K_{15}	(15)

Analysis of the problem commences by determining, at a given Eh and pH, which solid species is stable. The stable solid is that for which the base-line species, in this case Fe^{2+}, has its lowest concentration when the equilibrium expressions for the various solid-forming reactions are considered (reactions 6–15). After the most stable solid is established, the dominant aqueous species is determined from a similar analysis of the reactions involving only aqueous species (reactions 1–5), and the total aqueous species concentration of the element of interest is determined as a sum of the concentrations of all the aqueous species.

The code was tested in two runs conforming to the iron systems discussed by Garrels and Christ.[3] The two tests differ only in the complexing species assumed in the solution. The first test assumes the water contains only inorganic carbon at a level of 1×10^{-2} M (besides the iron species, of course), and the sulfur-containing reactions drop out of the system. Figures 1–4 present the plots and log file produced by EHPH for this test; Figure 5 is the comparison figure from Garrels and Christ.[3] The second run assumes the water contains only sulfur species, at a total sulfur species concentration of 1×10^{-1} M, and the $FeCO_3(s)$ reaction is thus eliminated. Figures 6–9 present the plots and log file for this case, and Figure 10, again from Garrels and Christ, is reproduced for comparison.[3]

There are some apparent differences between the comparable figures (Figures 6 and 10) for the second (sulfur) case that bear explanation. First, the $FeSO_4$ region does not appear on the Garrels and Christ[3] plot because this species was not considered in their analysis. Second, Figure 10 contains a number of lines marking the boundaries between the regions

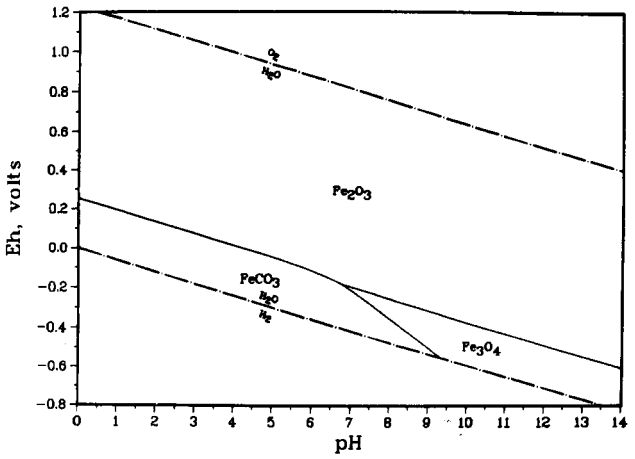

Figure 1. Stable solid species plot produced by EHPH for example run 1.

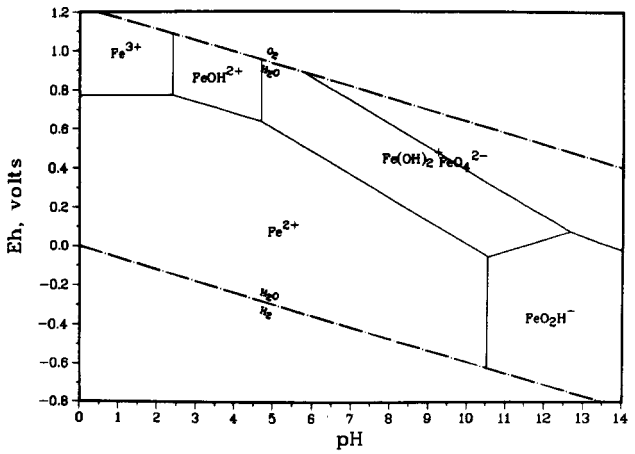

Figure 2. Dominant aqueous species plot produced by EHPH for example run 1.

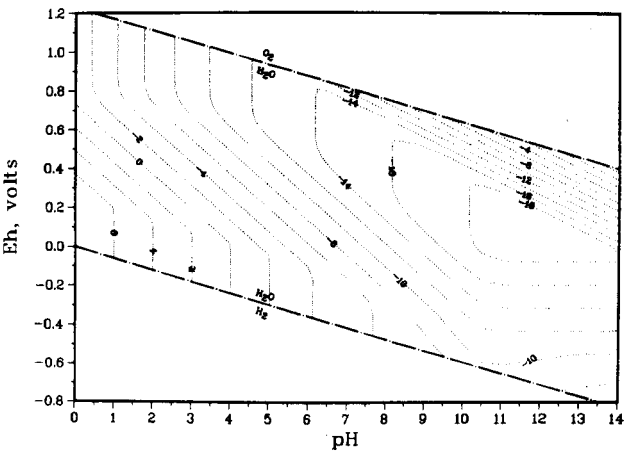

Figure 3. Aqueous concentration contours plot produced by EHPH for example run 1.

```
Plot: 636230
Date: TUE, APR 12 1983
Time: 16:04:07
T=    298.0
PHMAX= 14.0
PHMIN=  0.0
EHMAX=  1.2
EHMIN= -0.8
PH NODES=   25
EH NODES=   25

OPTIONS CHOSEN:
Echo species and water composition input
Print balanced reactions
Fe+2            F  -20300.0      -27.1
Fe+3            F   -2520.0      -70.1
FeOH+2          F  -55910.0      -23.2
Fe(OH)2+        F -186200.0        0.0
FeCl+2          F  -35900.0      -22.0
FeO2H-          F  -90600.0        0.0
FeO4-2          F -111000.0        0.0
*EOF                    0.0        0.0
Fe              F       0.0        6.5
FeO             F  -58400.0       12.9
Fe2O3           F -177100.0       21.5
Fe3O4           F -242400.0       35.0
Fe(OH)2         F -115570.0       19.0
Fe(OH)3         F -166000.0       23.0
FeS             F  -23320.0       16.1
FeS2            F  -36000.0        0.0
FePO4           F -272000.0       22.4
FeCO3           F -161060.0       22.2
FeSiO3          F -257000.0       20.9
Fe2SiO4         F -319000.0       35.4
FeSO4           F -198300.0       27.6
FeCl3           F  -80400.0       27.6
Cl              0.0000
S               0.0000
F               0.0000
Si              0.0000
C               0.0100
P               0.0000
Fe+2 = Fe+3 + e-                                LOG(K)     -13.0
Fe+2 + H2O = FeOH+2 + e- + H+                   LOG(K)     -15.5
Fe+2 + 2H2O = Fe(OH)2+ + e- + 2H+               LOG(K)     -20.2
Fe+2 + 2H2O = FeO2H- + 3H+                      LOG(K)     -31.6
Fe+2 + 4H2O = FeO4-2 + 4e- + 8H+                LOG(K)     -99.0
Fe+2 + 2e- = Fe                                 LOG(K)     -14.0
Fe+2 + H2O = FeO + 2H+                          LOG(K)     -13.6
2Fe+2 + 3H2O = Fe2O3 + 2e- + 6H+                LOG(K)     -24.6
3Fe+2 + 4H2O = Fe3O4 + 2e- + 8H+                LOG(K)     -33.2
Fe+2 + 2H2O = Fe(OH)2 + 2H+                     LOG(K)     -13.3
Fe+2 + 3H2O = Fe(OH)3 + e- + 3H+                LOG(K)     -17.0
Fe+2 + CO3-2 = FeCO3                            LOG(K)      10.7
OK,
```

Figure 4. log file for example run 1.

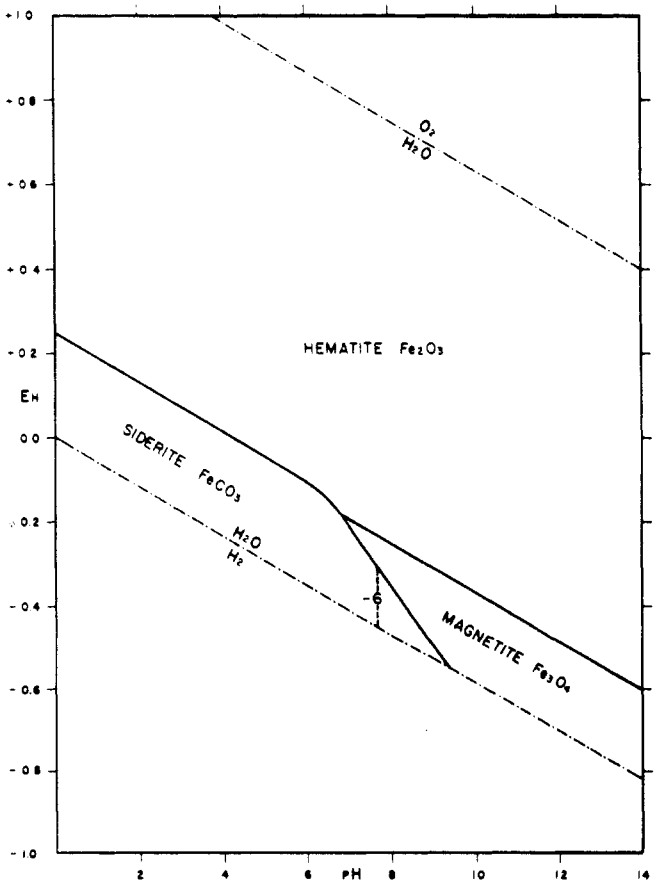

Figure 5. Comparison figure for example run 1. Reprinted with permission from ref 3.

of dominance of the various sulfur species (sulfate, sulfide, bisulfate, etc.) even where the iron-containing species has not

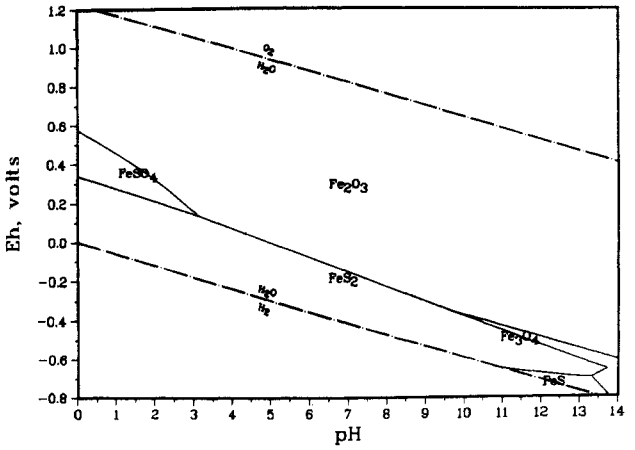

Figure 6. Stable solid species plot produced by EHPH for example run 2.

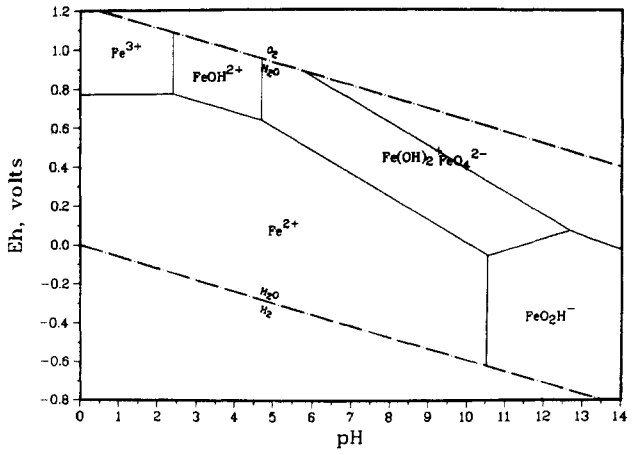

Figure 7. Dominant aqueous species plot produced by EHPH for example run 2.

changed. These lines are not plotted by EHPH. For example, the $FeS_2(SO_4^{2-})$ and $FeS_2(HS^-)$ regions in Figure 10 are incorporated in the FeS_2 region of Figure 6. When these extraneous lines are removed, the only difference between the two plots occurs in the regions designated for Fe_3O_4 and FeS and the high pH limit of the FeS_2 region. The explanation for this difference lies in the fact that the Garrels and Christ[3] plots do not include the reactions

$$Fe_3O_4 + 6HS^- + 2H^+ \rightleftarrows 3FeS_2 + 4H_2O + 4e^-$$

and

$$Fe_3O_4 + 3HS^- + 5H^+ + 2e^- \rightleftarrows 3FeS + 4H_2O$$

for which the Eh–pH expressions are respectively

$$Eh = -1.197 + 0.0298pH - 0.088 \log [HS^-]$$

and

$$Eh = 1.284 - 0.148pH - 0.088 \log [HS^-]$$

Had these reactions been included, the stable region shown for Fe_3O_4 between the FeS and FeS_2 regions would have appeared on the Garrels and Christ figure (Figure 10).[3]

CONCLUSIONS

The greatest limitation to the effective use of Eh–Ph analysis lies in the uncertainties in the data upon which the calculations depend. There are very few systems for which even the standard-state thermodynamic data are well established. For most systems, the existing standard data are both incomplete and characterized by considerable uncertainty, and data at

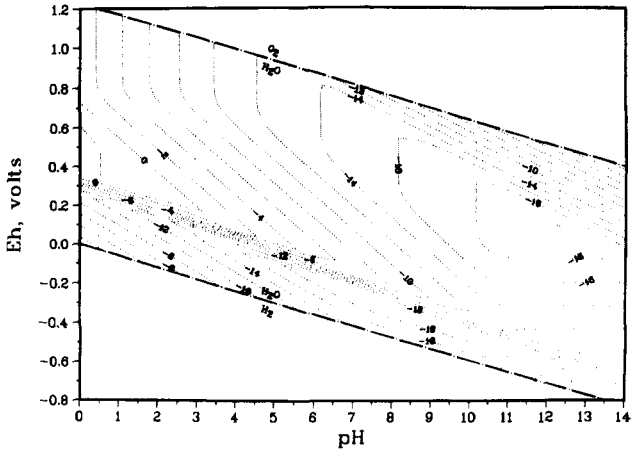

Figure 8. Aqueous concentration contours plot produced by EHPH for example run 2.

```
Plot: 270797
Date: TUE, APR 12 1983
Time: 16:09:20
T=      298.0
PHMAX= 14.0
PHMIN=  0.0
EHMAX=  1.2
EHMIN= -0.8
PH NODES=    25
EH NODES=    25

OPTIONS CHOSEN.
Echo species and water composition input
Print balanced reactions
Fe+2            F  -20300.0      -27.1
Fe+3            F   -2520.0      -79.1
FeOH+2          F  -55910.0      -23.2
Fe(OH)2+        F -106200.0        0.0
FeCl+2          F  -35000.0      -22.0
FeO2H-          F  -90600.0        0.0
FeO4-2          F -111000.0        0.0
#EOF                    0.0        0.0
Fe              F       0.0        6.5
FeO             F  -50400.0       12.9
Fe2O3           F -177100.0       21.5
Fe3O4           F -242400.0       35.0
Fe(OH)2         F -115570.0       19.0
Fe(OH)3         F -166000.0       23.0
FeS             F  -23320.0       16.1
FeS2            F  -36000.0        0.0
FePO4           F -272000.0       22.4
FeCO3           F -181060.0       22.2
FeSiO3          F -257000.0       20.0
Fe2SiO4         F -319000.0       35.4
FeSO4           F -198300.0       27.6
FeCl3           F  -80400.0       27.6
Cl             0.0000
S              0.1000
F              0.0000
Si             0.0000
C              0.0000
P              0.0000
Fe+2 = Fe+3 + e-                                  LOG(K)     -13.0
Fe+2 + H2O = FeOH+2 + e- + H+                     LOG(K)     -15.5
Fe+2 + 2H2O = Fe(OH)2+ + e- + 2H+                 LOG(K)     -20.2
Fe+2 + 2H2O = FeO2H- + 3H+                        LOG(K)     -31.6
Fe+2 + 4H2O = FeO4-2 + 4e- + 8H+                  LOG(K)     -99.0
Fe+2 + 2e- = Fe                                   LOG(K)     -14.0
Fe+2 + H2O = FeO + 2H+                            LOG(K)     -13.6
2Fe+2 + 3H2O = Fe2O3 + 2e- + 6H+                  LOG(K)     -24.6
3Fe+2 + 4H2O = Fe3O4 + 2e- + 8H+                  LOG(K)     -33.2
Fe+2 + 2H2O = Fe(OH)2 + 2H+                       LOG(K)     -13.3
Fe+2 + 3H2O = Fe(OH)3 + e- + 3H+                  LOG(K)     -17.0
Fe+2 + 8e- + 8H+ + SO4-2 = FeS + 4H2O             LOG(K)      38.5
Fe+2 + 14e- + 16H+ + 2SO4-2 = FeS2 + 8H2O         LOG(K)      84.0
Fe+2 + SO4-2 = FeSO4                              LOG(K)       0.5
OK.
```

Figure 9. log file for example run 2.

elevated (or reduced) temperatures are generally nonexistent. For many practical applications, analyses at temperatures other than 25 °C will be required. The EHPH code includes a mechanism for adjusting standard free energy data using entropies. This solution, of course, is effective only insofar as valid entropy data exist and then only over the range where the extrapolation remains reasonable.

The current version of the EHPH code is somewhat limited by the fact that activities rather than concentrations are computed. The modular nature of the code, however, will allow a correction to be implemented in a reasonably simple manner by adding a module to calculate activity coefficients, which will then be used to convert activities to concentrations.

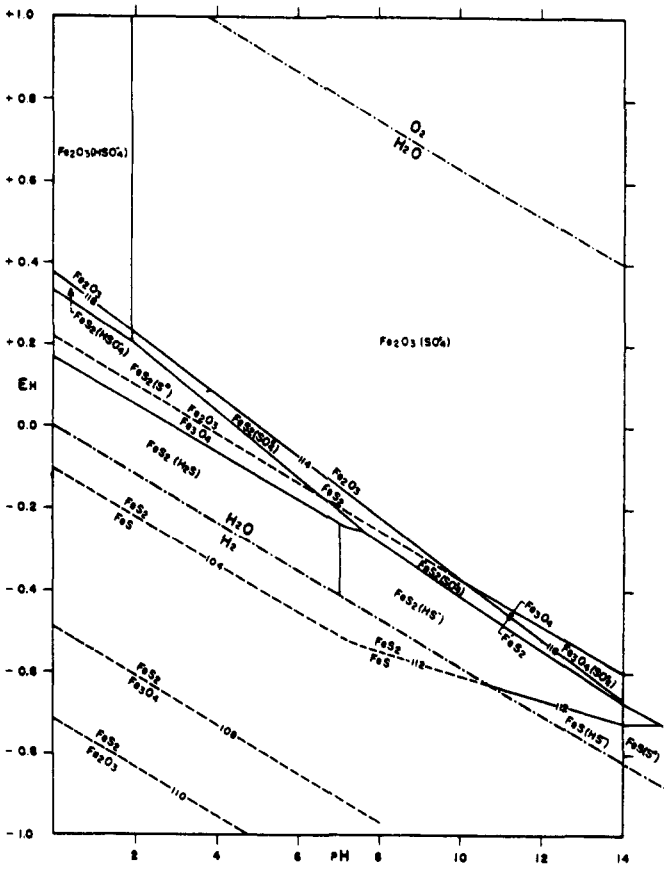

Figure 10. Comparison figure for example run 2. Reprinted with permission from ref 3.

Several theoretical approaches to correcting activities have been developed (e.g., extended Debye–Hückel theory and the Güntelberg approximation),[5] but the different approaches are applicable only under specific conditions. Since there is no single best approximation, the generality of EHPH has been preserved by not including an activity correction, while its utility has been guarded by structuring it so such a correction could be easily included, if desired, by a knowledgeable user.

These limitations aside, however, the EHPH code presents a useful tool in analyzing the thermodynamic relationships existing in an equilibrium chemical system. The code can be used to establish the expected aqueous and solid species for the system under given potential and pH conditions, as well as define how the solubility of the species under investigation changes with these conditions. Furthermore, there are portions of the code (e.g., the reaction-balancing algorithm) that may find applications in other programs dealing with chemical equilibrium systems.

Registry No. Fe, 7439-89-6; H_2O, 7732-18-5.

REFERENCES AND NOTES

(1) DISSPLA is a licensed software product of Integrated Software Systems Corp., San Diego, CA 92121.
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(5) Stumm, W.; Morgan, J. J. "Aquatic Chemistry", 2nd ed.; Wiley: New York, 1981; p 780.