Calculation of Potential-pH Diagrams of Metal-Sulphur Water Systems by Computer

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Construction of potential–pH diagrams manually is simple but time consuming since it involves a lot of repetitive and trivial calculations. Particularly for complicated systems, construction of such diagrams is difficult. This problem can be overcome by the use of digital computer.

Brief description of a computer program for the calculation of potential-pH diagrams for M-S-H$_2$O systems is presented.

INTRODUCTION

One of the most important contributions to corrosion literature in the past few decades has been the work of Pourbaix and his associates in the development of potential pH diagrams[1]. Various attempts have been made to increase the use of these diagrams by developing more convenient methods of calculation, Although potential-pH diagrams have so far been mainly used by metallurgists for corrosion studies, these diagrams can be useful for electro and hydrometallurgical studies. These diagrams may be used to summarize the stability (or instability) of sulphide minerals in contact with aqueous solutions of selected composition at a particular temperature. In fact these diagrams can be considered as useful to hydrometallurgists as Ellingham diagrams to pyrometallurgists. Unfortunately, for calculating equations used in constructing these diagrams, the procedure suggested is abstract and confusing. Because of labour involved in constructing those diagrams. especially of more complicated systems (like Metal-Sulphur-Water system) researchers have attempted to make use of the computor to construct potential-pH diagrams.

Computer Programs for Potential-pH Diagrams :

The determination of potential-pH diagrams with the aid of digital computers can be approached in different ways and many different programs can be written for that purpose. Because of its speed in handling tedious and repetitive calculation, the use of a computer will make possible the calculations of diagrams under various conditions of temperature and activities. Another very important feature of the computer is its ability to make logical decisions. The critical step in drawing a diagram is the selection of the stable equilibria and the relative position of the fields of thermodynamic stability. The computer has here an undeniable advantage on the human mind both in speed and reliability.

Two different programs have been developed at Columbia University[2]. A computer method of calculating potential-pH diagrams for simple metal-water system has been developed at the University of Nottingham, England[3]. This program was written in ALGOL and the graph plotting output was based on the National Physical Laboratory Scheme, Nittingham Operating System. It could handle only simple metal-water systems and cannot construct more complex diagrams such as metal-sulphur-water systems.

An improved method of calculation of potential pH diagram has been developed at the University of Florida[4]. This program can handle fairly complex metal-ion-water systems and makes use of the concept of 'Convexity' from Operations Research to determine areas of predominance of particular species. The program, however, does not actually construct the diagram but merely prints out the coordinates (in terms of potential and pH) of the set of points which constitute the corners of a convex polygon indicating the areas of predominance for a particular species. The potential-pH diagram is finally obtained by plotting the above points and connecting by straight lines.

A program for calculation of potential-pH diagrams for M S-H_2O systems has been written in FORTRAN-IV and run successfully at EC-1030 computer at Indian Institute of Technology, Bombay. The Zn-S-H_2O system provides a simple example of the application of this program. The various zinc and sulphur species considered are

shown in Table-1. Since generally computer line printers display only capital letters, it is necessary to develop a suitable convention for writing chemical formulae entirely on one line (no subscripts) and in capital letters. Any reasonable, internally consistent convention (such as in Table-1 Col. 2) may be employed provided it is suitable for the memory capabilities of the system being used.

TABLE 1

Data employed in computerized construction of the potential vs pH diagram for Zn - S - H_2O system at 25°C.

Species Considered		Gibbs free energy of formation (kcal/mole)	Assumed thermodynamic activity
Chemical notation	Computer notation		
Zn	ZN	0.000	1.000
Zn^{++}	ZN++	−3,184	0.001
ZnO	ZNO	−76.880	1.000
ZnO_2^{--}	ZNO2−−	−93.030	0.001
$Zn(OH)_2$	ZN (OH)2	−133.630	1.000
$Zn(OH)^+$	ZN (OH)+	−78.700	0.001
S	S	0.000	1.000
S^{--}	S−−	21.960	0.100
SO_4^{--}	SO_4−−	−177.340	0.100
$S_2O_8^{--}$	S2O8−−	−262.000	0.100
HS^-	HS−	3 010	0.100
H_2S	H2S	6.540	0.100
HSO_4^-	HSO4	−179 940	0 100
ZnS	ZNS	−47.400	1.000
$ZnSO_4$	ZNSO4	−208.310	1.000
$ZnSO_4.7H_2O$	ZNSO4.7H2O	−611.900	1.000

Input of Data :

Data is entered into the computer through cards: The first card enters the total number different metal-sulphur-water systems to be considered. For the first system, the second card enters the number of metal species (species containing metal atoms and which may or may not also contain hydrogen or oxygen atoms), the number of sulphur species (species containing sulphur atoms which may or may not have hydrogen or oxygen atoms) and complex species (species containing both metal and sulphur atoms which may or may not contain hydrogen and oxygen atoms). It also enters the number of different temperatures and different sets of activities of the various species under consideration for which diagrams have to be plotted. The next piece of data to be entered is the set of temperatures (in °C) for which diagrams are required. In the present example, (Zn–S–H_2O system),

No. of metal species = 6

No. of sulphur species = 7

No. of complex species = 3

as can be clearly seen from Table-1. Temperature is taken as 25°C and the activities are as given in Table-1. For the metallic species the necessary data like species name, elemental composition electrical charge, free energy of formation etc. are then given followed by different values of activities These are followed by data about species and complex species. The last card enters the maximum and minimum values of potential and pH to be considered, thus setting up the boundary of the diagram. It also enters the value by which potential is incremented, thus determining the accuracy of the diagram.

Chemical Equation Balancing and Equilibrium Line Determination :

When considering the possible formation of N different metallic species

$$\frac{N(N-1)}{2}$$

chemical equilibrium equations exist. The program takes all possible pairs of metallic species and balances the equations, in terms of water, hydrogen ions, electrons etc. A similar procedure is then used for the S species to tabulate the equilibrium line equations.

Areas of Predominance :

After determining the various equilibrium line equations, the program determines the areas of predominance for the various metal and sulphur species by using a subroutine. First, the metal species are considered. For a given value of potential E (max. to min.) from the main program, the subroutine considers the series of pH values (min. to max). It plugs in the values of E and pH representing a particular point in the diagram into the $\frac{N(N-1)}{2}$ equilibrium equations for the metal species, to find out the species which is predominant at that point. It uses a process of elimination for determining the stable species. Only the species which is predominat will always give a overall negative free energy change if it is involved as a product in a reaction. This procedure is repeated for all pH values. The stable metal species are stored in an array. Next, the entire procedure is repeated for the sulphur species and the stable sulphur species are stored in an array. Lastly the complex species are considered. The computer considers the reaction between the stable S species and the stable metal species to give the complex species and balances the chemical equation for the same. By scanning the diagram point and examining the free energy change for the reaction, the computer determines whether the complex is more stable than the individual metal and sulphur species The final diagram is printed line by line by a subroutine.

An expanded diagram can also be obtained by decreasing the range of potential and pH scanned by computer. This is particularly helpful to entangle the relationship between several compounds in a ternary system when the boundaries separating the fields of stability have slopes very close to one another.

Fig. 1 shows the flow chart giving a summary of the entire procedure followed.

1. Read Data
↓
2. Balance chemical equations for metallic species
↓
3. Use Nernst equation to determine equilibrium line equation
↓
4. Repeat steps (2) and (3) for sulphur species
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5. Call subroutine to determine stable metal and sulphur species
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6. Balance chemical equation between 'complex' species and stable metal and sulphur species
↓
7. Determine whether the complex is more stable
↓
8. Print out the diagram

Fig. 1 — Flow Chart.

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