PTA SYSTEM: A SOFTWARE PACKAGE FOR MICROCOMPUTER CALCULATION AND DISPLAY OF ACTIVITY-TEMPERATURE-PRESSURE PHASE DIAGRAMS*

By Robert G. Berman, and Thomas H. Brown
The University of British Columbia
Ernest H. Perkins, Alberta Research Council

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INTRODUCTION

In recent years, geologists have come to depend more and more on the use of phase diagrams to elucidate conditions of formation of a wide variety of rock types. Activity (A) diagrams are one type of phase diagram that has proved to be extremely valuable in providing a window to understanding processes involved in the genesis of economic mineral deposits. This report describes a recently completed IBM-compatible microcomputer program for the rapid calculation and display of a variety of such diagrams. With the development of accurate thermodynamic databases for minerals and aqueous species (see below), this program provides a powerful tool for understanding the physiochemical controls on formation of ore deposits. Copies of the program may be obtained by contacting the senior author.

GENERAL DESCRIPTION

Geo-Calc is a microcomputer software package consisting of programs for calculation of phase diagrams, thermodynamic databases for minerals and aqueous species, and auxiliary programs for viewing and printing of computed phase diagrams. The two main ingredients of the Geo-Calc package are the programs PTX-SYSTEM and PTA-SYSTEM. PTX-SYSTEM calculates complete pressure-temperature (P-T), temperature-composition (T-XH_2O-CO_2), and pressure-composition (P-XH_2O-CO_2) phase diagrams and has been previously described (Perkins *et al.*, 1986; Berman *et al.*, 1987; Brown *et al.*, 1988). PTA-SYSTEM, completed recently and described below, calculates activity-activity (A-A), temperature-activity (T-A) and pressure-activity (P-A) phase diagrams, where activity refers to the thermodynamic activity (or ratio and/or products of activities) of any mineral, gaseous or aqueous species.

The minimum hardware requirements for using the software are an IBM or compatible personal computer with 640K memory, and graphics card (CGA, EGA, or Hercules). Although a math coprocessor is not required, calculations with the PTA program proceed between six to ten times faster with a coprocessor installed. The PTA Version 2.0 release includes the programs described below.

SOFTWARE PROGRAMS

PTA: The PTA-SYSTEM program has been adapted for microcomputer use from mainframe programs that are available from E.H. Perkins. The major differences between the mainframe version and this implementation are that the three mainframe programs have been combined into one program, user input is simplified, several run-time options have been modified or removed, and the program generates and calculates each reaction separately rather than generating coefficients for all reactions before calculating any individual reaction. This last modification was necessary because of the limited memory available on most microcomputers for calculating and storing a large number of reaction coefficients

Execution times are dependent on hardware, the most important component being the math coprocessor speed. In general, AT-compatibles run approximately 1.5 to 2 times faster than XT-compatibles and 386 machines run up to 10 times faster than XTs. Computation time is also affected by run-time options, increasing dramatically when calculations are carried out in the vicinity of the critical point of water. Activity-activity diagrams are calculated many times faster than temperature-activity and pressure-activity diagrams because the Gibbs free energy functions need to be calculated only once in a given run. Total execution time, with a math coprocessor installed, should be in the order of seconds for systems with less than a hundred possible reactions, minutes for systems with several thousand possible reactions, and hours for systems with more than several hundred thousand possible reactions.

The output of PTA-SYSTEM can be plotted for visual representation of phase relations or inspected from a table. The program evaluates all possible reactions in the user-specified PTA space. At the user's option, each point of every reaction is tested for stability with respect to all other phases in the system, and metastable extensions are eliminated. If a curve is completely outside the pressure-temperature-activity limits of the diagram, any remaining reactions containing the metastable assemblage are removed from further consideration. Finally, all curves written to the plot file are labelled with stable assemblages. Run-time options include setting the pressure-temperature-activity limits of the diagram, the selection of ideal or non-ideal H_2O-CO_2 (only for systems that do not involve aqueous species), and the specification of fixed phase or species activities. The user can also specify that only curves stable in the presence of a given
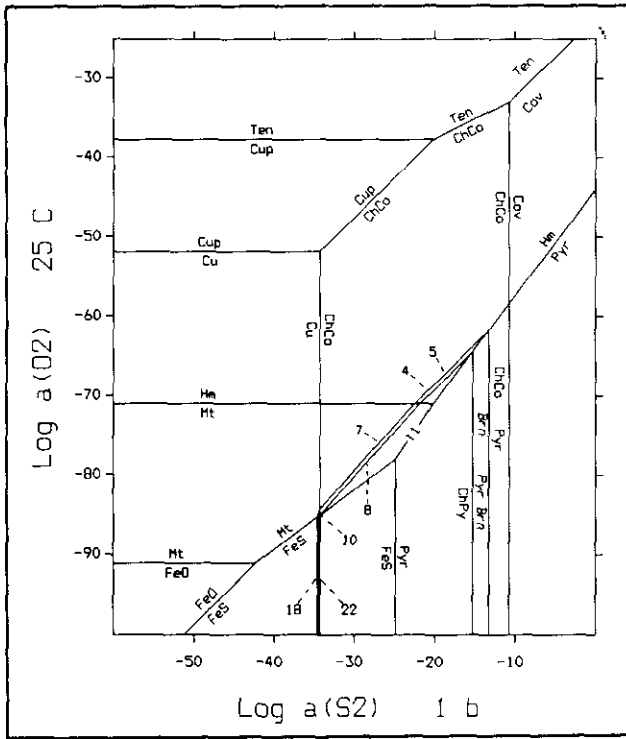
Figure 6-3-1. LASER plot of Log aS$_2$ vs. Log aO$_2$ diagram for the system Cu-Fe-S-O at 25°C and 1 bar. The unlabelled stability field in the lower centre of the diagram is that of bornite.

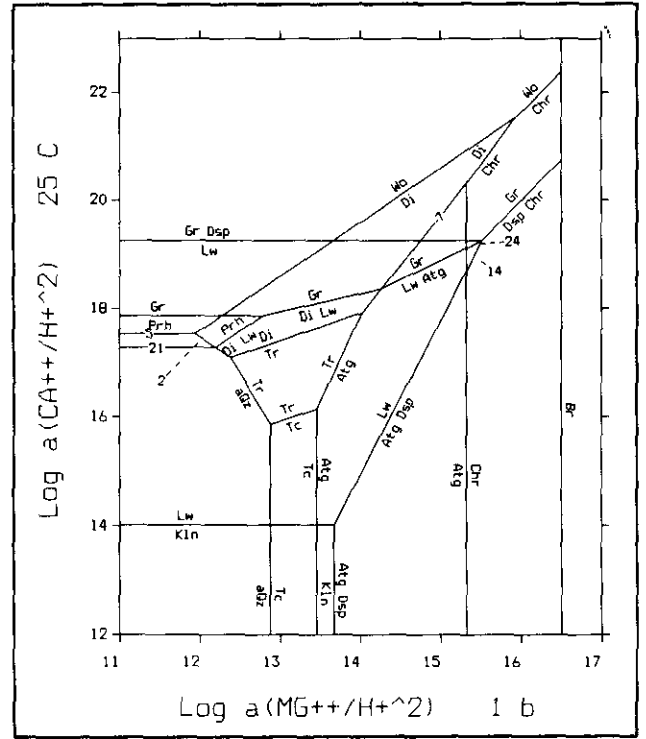Figure 6-3-3. LASER plot of Log aMg^{++}/(H$^+$)^2 vs. Log aCa^{++}/(H$^+$)^2 diagram for the system CaO-MgO-Al$_2$O$_3$-SiO$_2$-H$_2$O at 25°C and 1 bar.
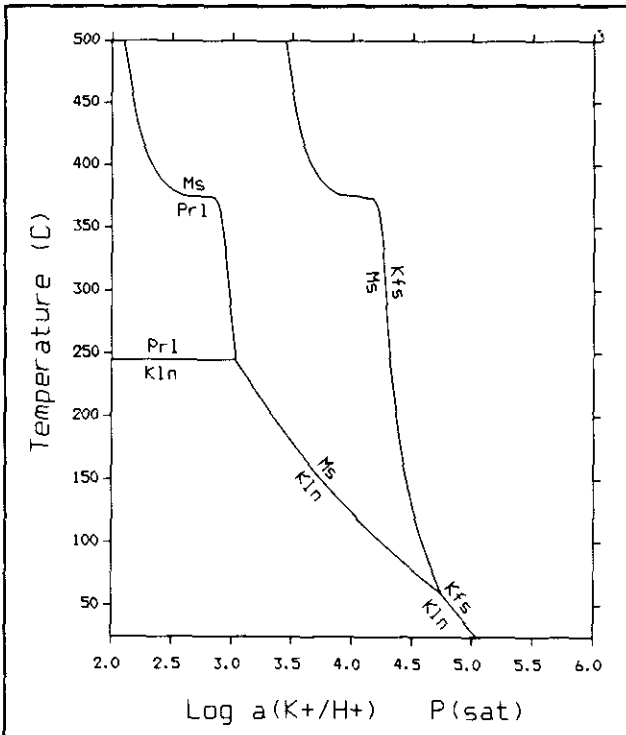
Figure 6-3-2. LASER plot of Temperature vs. Log aK$^+$/aH$^+$ diagram (projected from quartz) for the system K$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O with pressure fixed by the boiling curve of water.

phase or assemblage be computed, so that the stability fields of particular phases or assemblages can be readily identified.

Progress of the calculation can be followed in graphics or text mode. In graphics mode, each reaction curve is plotted on the screen as it is calculated, allowing the user to follow the search strategies and to see the phase diagram take shape. In text mode, calculations are summarized on a text screen which shows the current reaction being examined, the number of reactions already calculated, and an estimate of the percentage of reactions remaining to be calculated.

PTA-system allows one to calculate any phase diagram using the variables P, T, or A (the activity of any phase or species), and faithfully calculates equilibrium curves defined by the equality of Gibbs free energy of reactants and products of each equilibrium. The user should always be aware that the accuracy of calculated phase diagrams is a direct function of the quality of thermodynamic input data. The data distributed with this software are those presented by Helgeson et al. (1981) for aqueous species and those derived by Berman (1988) for minerals in the system Na$_2$O-K$_2$O-CaO-MgO-FeO-Fe$_2$O$_3$-Al$_2$O$_3$-SiO$_2$-TiO$_2$-H$_2$O-CO$_2$. Further details of the procedure used to derive this dataset are given by Berman et al. (1986).

Also included on the distribution discs is an alternate database for minerals derived by Berman et al. (1985). Although the 1988 database represents an update and improvement of this dataset, it is included in this package because several phases are present, notably zeolites, that are not present in the revised database. Note, however, that this database must be used in its entirety; phases from this dataset

cannot be used meaningfully with phases from the revised dataset.

PLOTS: This program displays graphical output on video monitors using a Hercules card or an IBM or compatible colour-graphics adapter (CGA) or enhanced-graphics adapter (EGA). PLOTS offers a quick way to preview plots on the screen prior to making hard copies with the PRINTER or LASER programs (see below).

LASER: This program makes high-resolution hard copies of the graphical output on HP-LASERJET-II printers with at least 1.5 MB of memory. Figures 6-3-1, 2 and 3 show examples of phase diagrams printed on the laser printer. Provisions have been made to allow variable line types and widths.

PRINTER: This program makes high resolution hard copies of phase diagrams on EPSON or compatible dot-matrix printers. The hard copies produced by PRINTER look similar to Figures 6-3-1, 2 and 3 except the resolution is lower than that produced by LASER.

CLEAN: The graphical output of PTA-system is often difficult to read because reaction labels overlap one another in any reasonably complex phase diagram. The program CLEAN improves the appearance of complicated phase diagrams on which the reaction labels overwrite one another. It either moves the labels to new positions or replaces the conflicting reaction labels with numbers and writes a list of reactions that correspond to the numbers to a separate file. The CLEANed plot (for example Figures 6-3-1, 2 and 3) can be viewed on the screen with PLOTS or on hard copies made with PRINTER or LASER.

LIMITATIONS AND FUTURE DEVELOPMENTS

The principal limitation of the present software package is that imposed by incomplete description of the thermodynamic properties of ore minerals and the plethora of aqueous species relevant to their genesis. The latter problem is being addressed by a variety of workers and much progress has been made recently in improving and extending equations of state for aqueous species to 600°C and 500 megapascals (Tanger and Helgeson, 1988) and in calculating equation of state parameters for dissociated and associated species (Shock and Helgeson, 1988).

H.C. Helgeson and coworkers have compiled a database for their SUPCRIT program that includes many ore minerals. These data (Table 6-3-1) have been combined with the refined data of Berman (1988) for common rock-forming minerals, and included in this version of the PTA software package. The only inconsistency that this combination of data introduces occurs with iron-bearing minerals, because the thermodynamic properties of magnetite and hematite are slightly different in the two databases. Future work will remove this inconsistency, in addition to expanding the scope of the data for ore minerals and refining thermodynamic properties using phase equilibrium data.

Another shortcoming of the present software is that the means for calculating an equilibrium distribution of aqueous species is not provided. Future work will address this limitation.

ACKNOWLEDGMENTS

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TABLE 6-3-1
MINERALS WHOSE THERMODYNAMIC PROPERTIES HAVE BEEN TAKEN FROM THE SUPCRIT COMPILATION OF HELGESON AND COWORKERS

Mineral	Formula
Acanthite	Ag_2S
Alabandite	MnS
Alunite	$KAl_3S_2O_{14}H_6$
Anglesite	$PbSO_4$
Anhydrite	$CaSO_4$
Azurite	$Cu_3C_2H_2O_8$
Barite	$BaSO_4$
Bornite	Cu_5FeS_4
Bunsenite	NiO
Celestite	$SrSO_4$
Cerrussite	$PbCO_3$
Chalcocite	Cu_2S
Chalcopyrite	$CuFeS_2$
Cinnabar	HgS
Covellite	CuS
Cuprite	Cu_2O
Ferrous oxide	FeO
Fluorite	CaF_2
Galena	PbS
Graphite	C
Halite	$NaCl$
Malachite	$Cu_2CH_2O_5$
Manganosite	MnO
Meta-cinnabar	HgS
Native copper	Cu
Native gold	Au
Native silver	Ag
Nickel	Ni
Pyrite	FeS_2
Pyrrhotite	FeS
Quicksilver	Hg
Rhodochrosite	$MnCO_3$
Siderite	$FeCO_3$
Smithsonite	$ZnCO_3$
Sphalerite	ZnS
Strontianite	$SrCO_3$
Sylvite	KCl
Tenorite	CuO
Witherite	$BaCO_3$
Wurtzite	ZnS

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