

SOFTWARE NOTICE

Program GIBBS: A generalized Gibbs method algorithm

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ABSTRACT

A program is described that performs generalized Gibbs method calculations. The program is menu driven and has applications in a variety of petrologic and phase-equilibria problems.

INTRODUCTION

Program GIBBS is a routine coded in FORTRAN that has been designed to perform generalized Gibbs method (Spear et al., 1982) calculations. The present program is the successor to the P-T PATH program of Spear (1986), which computed pressure-temperature paths from zoned garnets. The Gibbs method is a procedure that uses a Jacobian transformation to compute changes (i.e., finite differences) in a set of dependent thermodynamic variables, given the changes in a set of independent thermodynamic variables. The thermodynamic variables are the derivatives of T (temperature), P (pressure), μ (chemical potential), X (composition), and, if desired, M (the number of moles of a phase in an assemblage).

METHOD

A set of linearly independent equations among the thermodynamic variables is set up. These equations include (1) a Gibbs-Duhem equation for every phase in the assemblage; (2) a set of linearly independent relations written among the chemical potentials of the phase components of the phases in the assemblage; (3) a set of equations that relate the differentials of the compositions of the phases (dX) to the curvature of the Gibbs free-energy surface for the phase; and, if desired, (4) a set of mass-balance equations.

From the list of variables in the problem (P , T , and all μ , X , and M values), the user chooses a set of independent variables and specifies the increment of change for each independent variable. All other variables in the problem are necessarily dependent variables. The number of independent variables is determined by the variance of the system of equations. In problems that do not incorporate mass-balance equations, the variance of the system of equations is equal to the Gibbs phase-rule variance. In problems that do incorporate mass-balance constraints, the variance of the system of equations is 2, as required by Duhem's theorem.

The set of equations is solved for changes in the dependent variables as follows. The equations are arranged with the differentials of the dependent variables and their respective coefficients on one side of the equations and the differentials of the independent variables and their respective coefficients on the other side. In matrix form, this may be written:

$$AD = BI$$

where A and B are the matrices of dependent and independent coefficients, respectively, and D and I are the vectors of dependent and independent variables.

Premultiplication by the inverse of A (A^{-1}) yields

$$D = (A^{-1}B)I.$$

In practice, this operation is performed by Gaussian elimination and back substitution. The desired changes in the independent variables, the matrix D , may then be obtained for specified changes in the dependent variables, the vector I .

THERMODYNAMIC DATA BASE

Any internally consistent set of thermodynamic data may be used. The required data are entropy, volume, and heat capacity for each phase. Enthalpy data are not required because the enthalpies of reaction are inferred from the starting compositions of the minerals. Volume of solids is assumed to be independent of P and T . Ideal ionic mixing of solid solutions is assumed unless otherwise specified. Nonideal mixing models could be considered by coding the model into a subroutine.

The thermodynamic data base supplied with the program is taken from the recent compilations of Berman et al. (1985, 1987) and Berman (1988) with additional data as estimated by Spear and Cheney (1989). The current thermodynamic data base supports the system components SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , FeO , CaO , MnO , Na_2O , K_2O , H_2O , and CO_2 ; additional components may be added if desired. Entropy and volume of H_2O are computed from the Haar equation of state (Haar et al., 1979) and are interpolated from a table containing these values. Entropy of CO_2 is from Bottinga and Richet (1981). Volume of CO_2 and mixing of H_2O and CO_2 are computed using the equation of state of Kerrick and Jacobs (1981; see also Jacobs and Kerrick, 1981).

PROGRAM DESCRIPTION

Starting input to the program consists of a data set that specifies the chemical system, the mineral assemblage, a reference pressure and temperature, and the compositions and modes of phases in the assemblage at the reference P and T . This set of data is used as the reference conditions from which all changes in T , P , X , and M are calculated. The reference data set must represent an equilibrium mineral assemblage.

The program is menu driven, and several options are available. These include (1) routines to input and output information pertaining to a reference mineral assemblage, (2) routines to perform calculations of single increments of independent variables, (3) routines to draw contours in P - T space or in any X - Y diagram or to draw contours on ternary Fe-Mg-Mn diagrams, and (4) routines to perform automated calculations given an input file containing a list of the values of the independent variables to be incremented. In addition, there are several general options to change the mineral assemblage, to change the amount of output produced, to set and reset reference points, and to specify plotting parameters.

Output of the program includes a list of the values of all vari-

ables at the end of each step of the computations. The program also drives a Hewlett-Packard compatible plotter. Any pair of variables can be chosen by the user as axes for a plot. In addition, triangular FeO-MgO-MnO diagrams are supported. Plots may be drawn during execution of the GIBBS program or a file may be created that contains *P-T-X-M* information for later plotting.

There are two accessory programs in the package. The first is a program to transform an ASCII version of a thermodynamic data file into a direct access format that is read by the program (program DIRECT). This allows the thermodynamic data file to be modified by the user. The second accessory program plots results that have been saved on disk (program MODELPT). This latter program will generate plots of *X*, *M*, or *V* (volume) versus *T*; *X* versus radius of mineral produced; or triangular (FeO-MgO-MnO) diagrams.

The program is written in FORTRAN and is compiled using the Microsoft Optimizing FORTRAN compiler, v. 4.0. An IBM PC or compatible with 300 kbytes RAM is required. The program will run on machines with or without a math coprocessor, although execution speed is approximately seven times faster with a coprocessor. A plotter compatible with Hewlett-Packard graphics language (HPGL) is recommended. All source code is supplied with the program. The program is distributed on either three 360-kbyte or one 1.2-Mbyte floppy disks. A donation of \$25 is requested to defray the cost of shipping and handling.

APPLICATIONS

The power of the GIBBS program lies in the fact that the choice of independent variables is completely arbitrary. Therefore, a variety of petrologic problems may be addressed by this method. Examples of the types of problems that have been examined include (1) calculation of metamorphic *P-T* paths from zoned garnets (Spear and Selverstone, 1983), (2) analysis of the phase equilibria of metamorphic systems (e.g., Spear, 1988a; Menard, 1989), (3) analysis of the effects of fractional crystallization on the evolution of metamorphic mineral assemblages (Spear, 1988b), and (4) calculation of a petrogenetic grid for pelitic schists (Spear and Cheney, 1989).

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