Algorithmization of the Numeric Equilibrium Modeling of Dynamic Geochemical Processes

Yu. V. Shvarov

Faculty of Geology, Moscow State University, Vorob'evy gory, Moscow, 119899 Russia
Received December 11, 1997

Abstract—A method is proposed for the algorithmic description of dynamic models of geochemical processes. It is assumed that the process modeled can be approximated by a sequence of equilibrium states of the geochemical system. The model of the process consists of the rules of transition from one equilibrium state to another; the states could differ both in composition and in temperature values, pressure, and potentials of perfectly mobile components. The realization of several models, from "degree of reaction progress" to "sequential flow reactors," is demonstrated in the thermodynamic modeling HCh program package. The proposed method of describing the dynamic models is designed for use by researchers without special knowledge in programming.

INTRODUCTION

Thermodynamic modeling has long been a common method of investigation in geochemistry. Owing to the increasing capabilities of personal computers and the appearance of numerous programs allowing efficient calculation of the equilibrium compositions of chemical systems approaching natural systems in complexity, thermodynamic modeling becomes universally accessible. In addition to simple investigations of equilibrium states of geochemical systems, the methods of thermodynamic modeling allow the study of some types of dynamic processes that could be approximated as a sequence of equilibrium states of a thermodynamic system. Examples of such models are the well-known models of "degree of reaction progress" [1] and "sequential flow reactors" [2, 3].

Many natural geochemical processes might allow construction of such equilibrium dynamic models, which would describe them with reasonable accuracy and in sufficient detail even if the processes are not strictly reversible. However, the choice of a model is often determined not by the properties of the object studied and personal wishes of the researcher, but by programs available for modeling. As a result, available computer programs may be inappropriate for the researcher's conceptual model of the process. In this case the researcher is forced either to model the process manually, only using the available software to calculate individual points, or to undertake special efforts to create the necessary software. Since both ways require considerable finances and time, there is no great diversity in equilibrium dynamic models for geochemistry.

This paper presents the results of work that was aimed on the development of software for the IBM PC AT, which would allow efficient modeling of natural and chemical technological processes occurring in an aqueous solution, a gas mixture, solid or liquid (not aqueous) solutions, or in pure phases in open and closed chemical systems. We propose a method to describe dynamic systems with chemical reactions, which allows us to include a wide range of practically solvable problems, is characterized by simple implementation, and can be easily incorporated into available program packages used for thermodynamic calculations. This method was tested and incorporated into the HCh package, which we designed for thermodynamic modeling.[1] One of the major requirements for the methods of dynamic model description was the simplicity and accessibility for those researchers who are not specialists in programming, but who wish to apply their own conceptual models of dynamic processes. At first glance, such a restriction seems to be contradictory. However, the approach presented in this paper allows a user to construct various equilibrium models of dynamic processes by a single tool, the package HCh for thermodynamic modeling.

HCh: A PROGRAM PACKAGE FOR THERMODYNAMIC MODELING

The possibility to build a user-defined local equilibrium model of a dynamic process is realized in a special module of HCh. It is not independent of other modules, because it uses stoichiometric, thermodynamic, and other parameters of the system under question. Because of this, before the detailed description of the module, it is necessary to characterize the whole package, whose functional scheme is shown in Fig. 1.

HCh consists of three main parts: the thermodynamic database UNITHERM including the parameters of components of aqueous solution and pure substances: gases, minerals, and liquids necessary for cal-

---

[1] The package's name is an abbreviation of the word HydroChemistry, because it was initially designed for use in hydrochemistry.
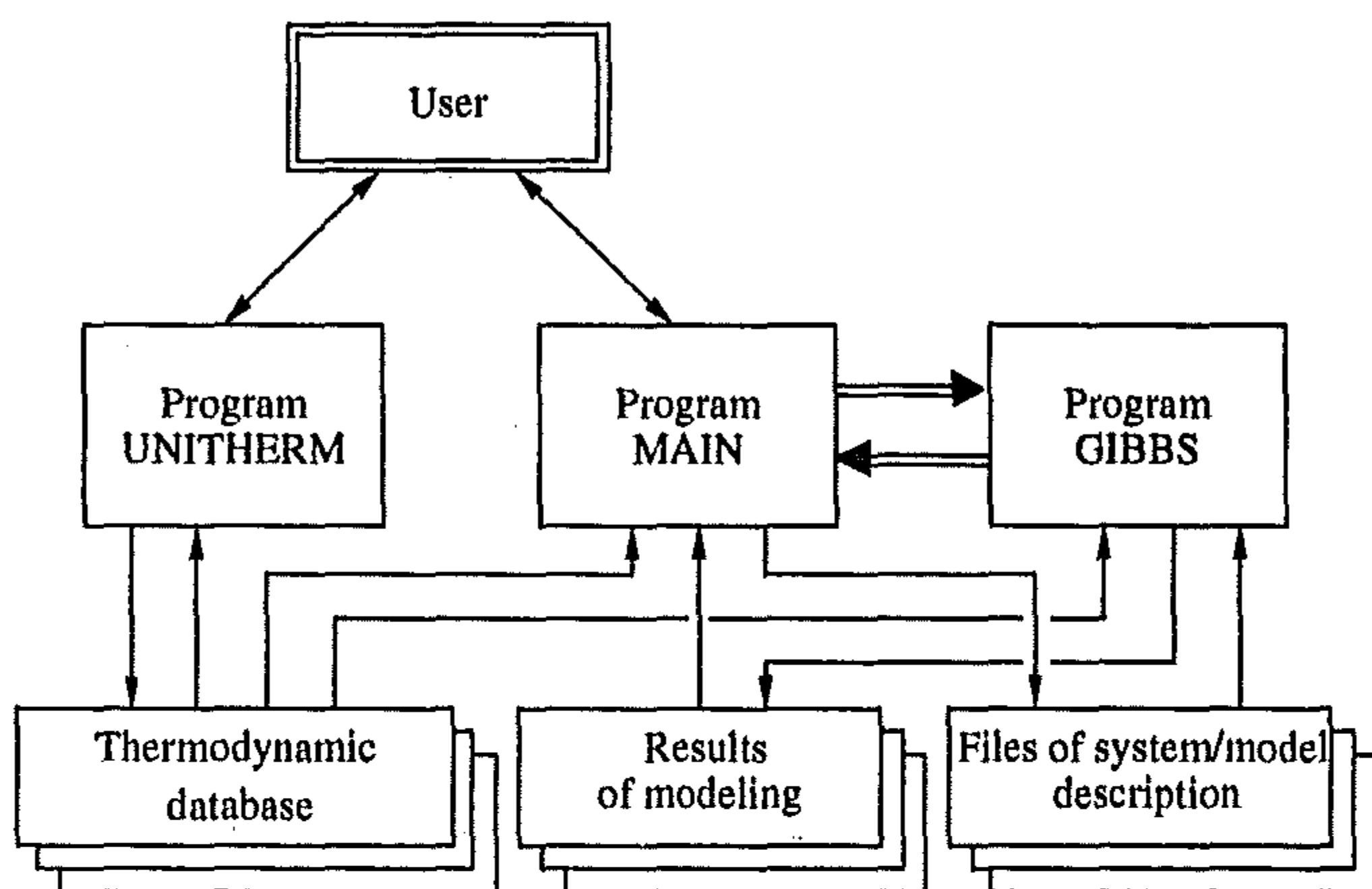
Fig. 1. Interactions of components of the HCh package. Single-line arrows show directions of information transmission and double line arrows, control transmission.

culate their Gibbs free energies; the program MAIN designed for maintaining calculation processes (creating files with the description of chemical systems, format of input data and the data themselves used as initial for equilibrium calculations, and others); and the program GIBBS, which calculates equilibrium composition in the system using the minimization of Gibbs free energy of the system as a criterion for equilibrium (necessary thermodynamic information is taken directly from the database).

The thermodynamic database UNITHERM is controlled by a separate program of the same name and includes the thermodynamic properties of water, aqueous species, and pure phases: gases, liquids, and solids. The thermodynamic properties of water are described by the model of Haar–Gallaher–Kell [4] and aqueous species are described either by the Helgeson–Kirkham–Flowers [5, 6] formalism or by the model of complex formation by Ryzhenko–Bryzgalin [7, 8]. The properties of other components in the database are given mainly by equations of their heat capacities (up to four phase transitions are allowed). Temperature and pressure values are limited in the calculation of water-bearing systems by the calibration ranges of the models involved: 0–$1000°C$ and 1–5000 bar. UNITHERM has a simple and friendly interface and allows the construction of user databases oriented for particular applications.

At least two files are necessary for the GIBBS program to calculate the equilibrium composition of a chemical system. The first is a System file, containing the stoichiometry of all possible phases and solution species in the system and the parameters necessary to account for the nonideality of their properties. (The System file is generated by MAIN on the basis of parameters from the UNITHERM database.) A Blank file, containing formats of data used to specify the bulk composition of the system, created interactively by MAIN, is the second. These include types of perfectly mobile components, inventory of product substances,

and units used to specify their amounts. If a Blank file is used as an input for GIBBS, the latter accepts from the user the values of temperature, pressure, and bulk system compositions and calculates equilibrium for each of the compositions, i.e., equilibrium calculations are executed in the interactive mode.

Input files (files of the third type) may contain up to three bulk system compositions, including, when necessary, potentials of perfectly mobile components. These files are also normally created interactively by MAIN, although it is possible to perform this task automatically. If GIBBS accepts an Input file at the beginning, it calculates equilibria for all compositions from this file with the user-defined values of external parameters, temperature, and pressure.

Finally, GIBBS can accept one more Control file, which maintains the program, omitting dialogue with the user during the modeling. Control files are also created interactively by MAIN and can contain full descriptions of dynamic models designed by the user. The work of MAIN to create, view, edit, and maintain in other ways controlling files is realized by a separate module, which is also called Control. The proposed method for the formation of equilibrium dynamic models of geochemical processes can be illustrated in detail by examples of work with this module, which are given below.

CONTROL: A MODULE FOR DESCRIPTION OF DYNAMIC MODELS[2]

HCh provides the capability of describing local equilibrium dynamic models. There are two user-available tools for this purpose: expressions and conditions. Expressions allow the user to define formulas (using all arithmetic operators and functions) for the calculation of temperature, pressure, potentials of perfectly mobile components (for open systems), and bulk compositions of the system, i.e., using all equilibrium parameters. Expressions may be scalar or vector depending on the type of parameters defined by them. The user is free to insert into expressions any numeric constants and some variables, which are displayed on the screen at each specific case (variables are described below). Expressions are entered by the user in regular notation.[3] The program converts expressions into the inner code using the reverse Polish notation, which is then used by the program for calculations. A condition is composed of two expressions connected by one of the comparison operators, equality or inequality, and allows one to

[3] In algorithms, the equal sign is often used as an *assignment* operator. For example, $i = i + 1$ means that the value of variable i is increased by one. In all the following formulas for the calculation of variables and vectors, it is used in this way. However, in *conditions* the equal sign is used as a comparison operator.

define the duration of iterative calculations of chemical equilibria by the GIBBS main modules.

Since the modeling of any process within the approach proposed consists in the cyclic repetition of calculations of a system's equilibrium compositions as input parameters change, the description of such a calculation procedure requires the use of the concept of a cycle. In order to attain maximum simplicity and convenience in the presentation of the calculation algorithm, a graphical scheme of the cycle used for model calculation is displayed on the screen. The user can view and edit in the interactive mode any block of this cycle including initialization, changes in conditions, and the test for finish conditions. In order to illustrate real steps executed by the user to build the calculation algorithm, Fig. 2 shows the diagram of a cycle as it appears on the screen.

Selecting a necessary block on the screen, the user can set corresponding model parameters. Receiving parameters for each block from the user, the program marks the block on the screen by the symbol "√" provided there is no error in the user's input. Following is the complete description of block parameters.

• Block Set Initial Composition: $i = 0$:

(a) Temperature (°C): an expression for parameter T is user-defined; only numeric constants are allowed here.

(b) Pressure (bar): an expression for parameter P is user-defined; in addition to numeric constants, variable T defined in point (a) is allowed.

(c) Potentials of perfectly mobile components may be specified as functions of T and P; these expressions do not appear if the system modeled is closed or the respective potentials are defined previously in input files describing the chemical system.

(d) Bulk composition of the system: a vector expression describing initial bulk composition for the model. Operands in this expression are vectors defined by the user symbolically as [1], [2], or [3], where the number denotes one of the bulk compositions from the input file. In vector expressions, multiplication of a vector by a scalar (numeric constant or variable) and the summation of vectors are permitted.

Note that the block of cycle initialization is not necessary and in some cases may be not defined (see Example 1 below).

• Block Recalculate Composition: $i = i + 1$:

(a) Temperature (°C): an expression is defined to calculate temperature at step i using previously defined (on the previous step) variables T, P (that is, if cycle initialization was not omitted by the user), and i, which is the current step number. It is evident that temperature can be defined recurrently.

(b) Pressure (bar): the rules are similar to those for temperature except for the possibility to use variable T without any limitations, because its current value is defined in point (a).
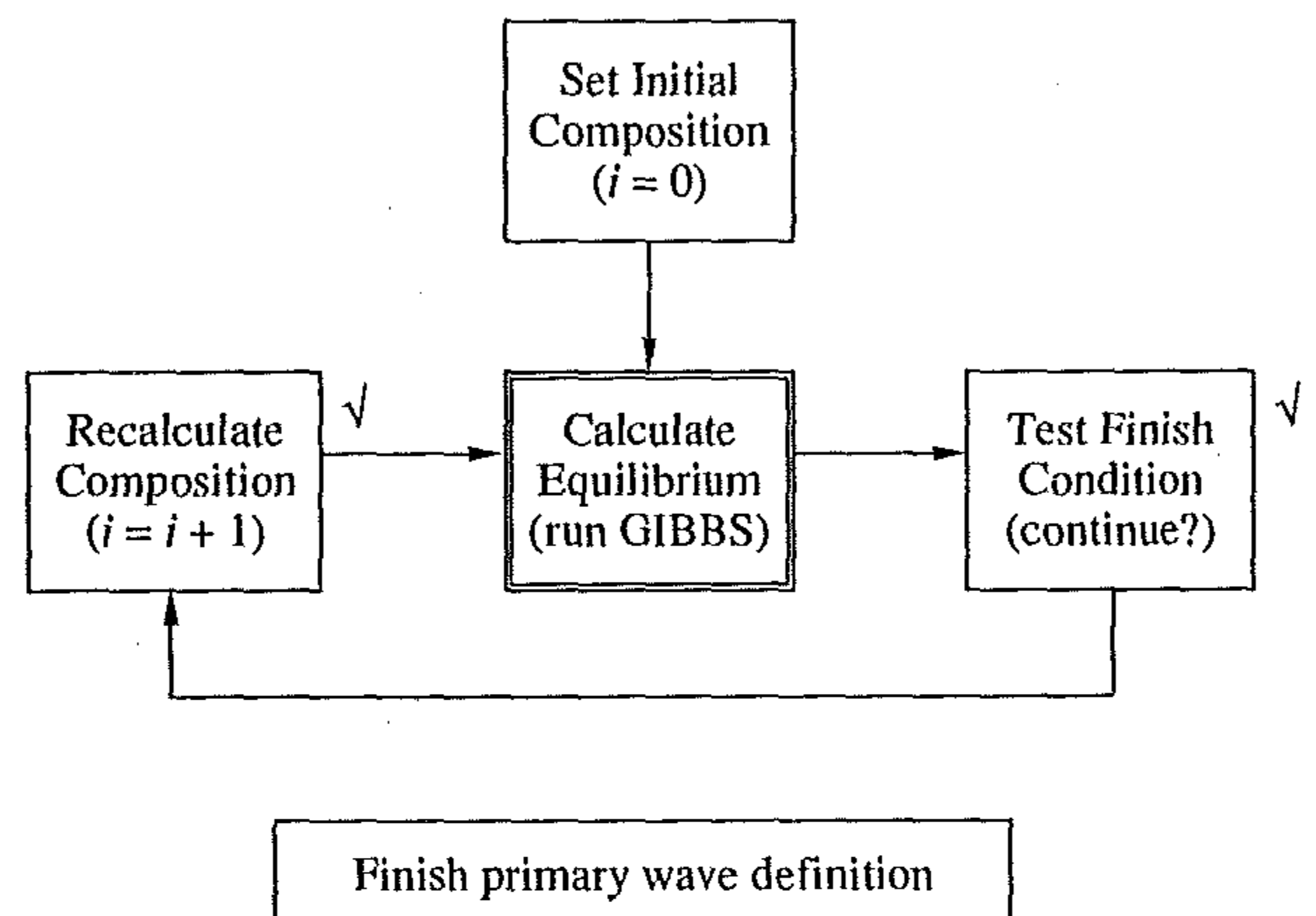
Diagram of PRIMARY WAVE computation ($N = 0$)

Fig. 2. Diagram of a cycle describing the algorithm of primary wave calculation. See text for further explanation.

(c) Potentials of perfectly mobile components (if necessary); variables T, P, and i (current values) are permitted.

(d) Bulk composition of the system (vector expression): in addition to vectors [1], [2], and [3] (i.e., vector constants from the input file), it is possible to use the symbols [*], [A], [S], [L], and [G] as vector variables, which denote, respectively, bulk composition of the equilibrium system from the previous step, and bulk compositions of its aqueous, solid, liquid (not aqueous), and gas parts; this allows the use of recurrent expressions for the redefinition of bulk compositions of the system.

Note that the recurrent computation of system composition is possible only if the initialization block was not skipped by the user.

• Block Calculate Equilibrium is used to define GIBBS options (nonstandard conditions); this possibility is rarely used and is not described here.

• Block Test Finish Conditions: the user defines the condition of halting the computation process; two types of conditions are permitted: "continue calculation, while…" and "stop calculation, if…," where the ellipsis stand for user-defined conditions. The definition of a condition includes two scalar expressions connected by one of the comparison operators: "<" (less than), "<=" (less than or equal to), "=" (equal to), ">=" (greater than or equal to), ">" (greater than), or "<>" (not equal to).

The above-described possibilities are sufficient for the construction of models of various types. The following two examples illustrate a user's actions in the definition of a model.

Example 1: Calculations of diagrams, investigation of chemical interactions by the method of the degree of reaction progress, etc. Let us suppose that the researcher is interested in the results of interaction

between an aqueous solution of some composition with given rocks in various rock/water proportions (say, from 10^{-5} to 10^{+5} kg of rock per 1 kg of water at a step of one order of magnitude), where $T = 300°C$ and $P = 500$ bar. In this case, the user prepares files in the usual way to characterize the chemical system under question and inserts two bulk compositions into the Input file: the compositions of the aqueous solution and the rock (1 kg each). After that, the Control file is formed in the following manner (in this and the following examples, all information entered by the user is shown in bold-face):

- The initialization block is not used
- Block Recalculate Composition:

  $T = 300$

  $P = 500$

  $[*] = [1] + [2] *10^{\wedge}(i - 6)$

- Block Test Finish Conditions:

  Finish computation if $i = 11$

The Control file is complete. To obtain calculation results, it is sufficient to pass this file to GIBBS. Note that this example requires the calculation of 11 compositions, i.e., the cycle is composed of 11 steps. Since i (step number) changes from 1 to 11, in the expression for the amount of rock, the exponent $(i - 6)$ changes from -5 to $+5$, as required by the conditions of the problem. If it is necessary to describe this interval with a smaller step, for instance, by a half order of magnitude, the exponent $(i - 6)$ should be replaced by $(i/2 - 5.5)$ and calculations should be finished at $i = 21$.

Example 2: Processes occurring in an unchanged environment. An example of a process occurring in an unchanged environment is the cooling of ore-transporting fluid ascending through a fracture. Although in this process temperature and pressure decrease, the environment does not change in the sense that the process can be described by changes occurring in the first portion of the solution, because all the later portions will pass the same evolutionary stages precipitating the same amounts of matter on the fracture walls (that is, if the effects of chemical interactions between the solution and enclosing rocks or previously deposited material may be ignored).

Let us assume that at some depth, at a temperature of 300°C and vapor-saturation pressure for this temperature, pure water comes into contact with a rock of known composition and attains chemical equilibrium with the rock. The solution (saturated with respect to the initial rock) then ascends through a fracture and precipitates its mineral loading, owing to the decrease in T and P. The problem is to determine the mineral composition of the newly formed vein. To solve the problem, two compositional vectors are entered into the Input file: the first one corresponds to pure water and the second, to initial rock (1 kg each). After that, the

model can be defined (in this example, our comments are given after the symbol #):

• Block Set Initial Composition:	# Determination of the composition of initial solution
$T = 300$	# Temperature at the initial depth
$P = 0$	# "0" means the pressure of vapor saturation
$[*] = [1] + [2] \times 100$	# The rock/water ratio is 100
• Block Recalculate Composition:	# Determination of the precipitating minerals
$T = T{-}2$	# Temperature decrement is 2°C
$P = 0$	# Vapor saturation pressure at the new temperature
$[*] = [A]$	# Only solution ascends
• Block Test Finish Conditions:	
Continue while $T > 0$	# Till complete cooling

The Control file is ready. On the basis of these instructions GIBBS yields an array of 150 compositions presenting (from bottom to top) changes in the mineral composition of the vein modeled.

However, in the general case, the conditions in the zones of chemical reactions may change with time. The first stage of interaction (calculated, for example, by the above procedure) results, by and large, in changes in the chemical composition of the reaction environment, and subsequent interaction stages will proceed under different conditions and may lead to other results. This is also true for any subsequent step of interaction. Thus, a user-defined algorithm for process modeling must provide the repeated execution of a calculation procedure similar to that described above, so that the result of each interaction step can be used to set the initial condition for the next one. The solution of this problem is in the description of another external cycle, defining rules for the use of modeling results obtained on the previous step. Each interaction stage will be called hereafter a "wave," which is a common notion in the literature on the modeling of hydrothermal processes. Thus, the above simple cycle is a primary wave, because it usually describes the filtration of the first solution portion through unaltered rock. The HCh package allows the user to describe a secondary wave in a simple and understandable way. It is important that, although the secondary wave is described only once in the model, the number of such waves is arbitrary.

The diagram for the description of the secondary wave is displayed on the screen and it is identical to the diagram of the description of the primary wave (see above), except for the title. Changes in the defining of variables are related only to the increasing number of variables available for the calculation of expressions (all variables used in the description of the primary

wave are also permitted here). The additional variables are the following:

N is the wave number (secondary waves are numbered starting from one, while the primary wave is always zero). Any parameter of the system may be described as a function of the wave number.

{*}, {A}, {S}, {L}, and {G} are, respectively, the bulk composition of the whole system and its aqueous, solid, liquid (not aqueous), and gas parts obtained on the same step of the previous wave. These vectors can be used only to specify the bulk composition of the system.

Another additional expression necessary for the description of the secondary wave defines the condition of model finishing (constraining the number of waves). It is defined in the same way as the cycle finish condition.

These additional features are sufficient to create a wide class of dynamic models for processes occurring in an initially isotropic environment.

Example 3: Modeling by the method of sequential flow reactors. It is necessary, for instance, to study the process of interaction of a rock of some composition with an aqueous solution during its filtration. To solve this problem, two bulk compositions must be provided to the Input file: the solution of a certain composition and the initial rock. The description of the respective dynamic model is as follows:

Primary wave

• Block Set Initial Composition:

$T = 25$ # Surface conditions are chosen for the process
$P = 1$

[*] = [1]   # Initial solution

• Block Recalculate Composition:

$T = T$ # Isothermic system
$P = P$ # Isobaric system
[*] = [A] + [2]   # Interaction solution–initial rock

• Block Test Finish Conditions:

Continue while $i < 50$ # Let 50 blocks suffice

Secondary wave

• Block Set Initial Composition:

$T = 25$ # Temperature and pressure do not change
$P = 1$

[*] = [1]   # Initial solution is the same

• Block Recalculate Composition:

$T = T$ # Isothermic process
$P = P$
[*] = [A] + {S}   # Interaction solution–altered rock

• Block Test Finish Conditions:

Continue while $i < 50$ # The secondary wave is not longer than the primary wave

• Constraint on the number of waves:

Continue while $N < 100$ # Sufficient as an introductory example

Receiving such a Control file, GIBBS calculates more than 5000 compositions of the system, which describe the results of interaction at various points along the filtration path (parameter i) and at various moments of time (parameter N).

Example 4: Inhomogeneous initial conditions and regimes. It is easily seen that the possibility to change both intensive and extensive equilibrium parameters allows the construction of combined models with conditions varying in space (parameter i) and time (parameter N). Moreover, if the initial inhomogeneity of the medium can be described analytically, similar dynamic models can be constructed readily for such processes. Continuous changes in the initial conditions and parameters of models (for instance, block size) can be easily specified within the proposed method, because, in addition to arithmetic operators, expressions may contain functions EXP (exponential function), LOG (natural logarithm), and SQR (square root), which allow application of polynomial and other classes of approximations of real distributions.

However, changes in the parameters of geologic environments are not always continuous. For instance, an abrupt change in the composition of enclosing rocks along the filtration path of ore-bearing solutions may serve as a geochemical barrier, which is of primary interest to a researcher. The proposed method of dynamic modeling allows implementation of such discontinuous functions. This possibility is realized in the module Control, which allows the use of conditions in parentheses as scalar operands in any expression along with constants and variables. Such an operand takes a value of one if the condition is true or nil in the opposite case.

Let us assume that before the beginning of filtration, there is a sharp boundary between two different rocks and it is necessary to solve the problem of Example 3 by the method of flow reactors. This task is accomplished by the following changes in the model: (1) a third composition is inserted into the Input file corresponding to the new rock and (2) in the block Recalculate Composition of the primary wave the expression [A] + [2] is substituted by [A] + [2] * ($i <= 25$) + [3] * ($i > 25$).

Another example of inhomogeneity in a geochemical system is abrupt changes in the composition of infiltrated solution, for example, the change of its source owing to tectonic movements or the cessation of liquid waste pumping into a bed (for research on rehabilitation processes). Changes in conditions of such a kind

are also easily modeled by the proposed techniques, because calculations can be paused at the end of any wave and the user is able to change the composition of initial solution in the Input file and then continue modeling with new parameters.

The above examples far from exhaust the diversity of dynamic models which can be constructed using the proposed techniques. Although the examples are related only to the simulation of hydrothermal systems, models for other processes can be built in a similar way, such as those occurring with the participation of gases or melts including reactions of condensation, crystallization, ion and isotope exchange, and other processes, provided they allow a local equilibrium approximation.

CONCLUSION

A considerable number of programs are currently available for the local equilibrium modeling of dynamic processes. A common drawback of all these models is that the user cannot go beyond the scope of a specific model realized by the particular program. The proposed approach allows the user not only to apply the existing models but also construct new ones including those that are outside the author's expertise.

To the author's knowledge, there is no work on the generalized description of algorithms for the thermodynamic modeling of geochemical processes. Although Chudenko *et al.* [9] mentioned that the BASIC-like description of algorithms was implemented into the SELECTOR program, no detail was given as to the possibility of the construction of dynamic models on this basis. It is possible that the authors of SELECTOR are also working in this direction.

The concept of local equilibrium is now the most common approach for the thermodynamic modeling of geochemical processes. An increasing number of researchers are participating in such investigations and are providing new ideas on various ways of local equilibrium approximations of natural processes. As a result, the development of necessary mathematical software is outstripped by the demands of this scientific realm. The author hopes that the method described in this paper will mitigate such a discrepancy.

REFERENCES

1. Helgeson, H.C., Evaluation of Irreversible Reactions in Geochemical Processes Involving Minerals and Aqueous Solutions. I. Thermodynamic Relations, *Geochim. Cosmochim. Acta*, 1968, vol. 32, no. 8, pp. 853–877.

2. Fritz, B., Etude Thermodynamique et Simulation des Reactions Entre Mineraux et Solutions. Application a la Geochemie des Alterations et des Eaux Continentales, *Mem. Sci. Geolog.*, 1975, no. 41.

3. Fouillac, C., Michard, G., and Bocquier G., Une Methode de Simulation de l'Evolution des Profils d'Alteration, *Geochim. Cosmochim. Acta*, 1977, vol. 41, pp. 207–213.

4. Kestin, J., Sengers, J.V., Kamgar-Parsi, B., and Levelt Sengers, J.M.H., Thermophysical Properties of Fluid H_2O, *J. Phys. Chem. Ref. Data*, 1984, vol. 13, no. 1, pp. 175–183.

5. Helgeson, H.C., Kirkham, D.H., and Flowers, G.C., Theoretical Prediction of Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures. IV, *Am. J. Sci.*, 1981, vol. 281, no. 6, pp. 1249–1515.

6. Tanger, J.W. and Helgeson, H.C., Calculation of Thermodynamic and Transport Properties of Aqueous Species at High Pressures and Temperatures: Revised Equations of State for Standard Partial Molal Properties of Ions and Electrolytes, *Am. J. Sci.*, 1988, vol. 288, no. 1, pp. 19–98.

7. Ryzhenko, B.N., *Termodinamika ravnovesii v gidrotermal'nykh rastvorakh* (Thermodynamics of Equilibria in Hydrothermal Solutions), Moscow: Nauka, 1981.

8. Bryzgalin, O.V., Estimation of Thermodynamic Dissociation Constants of Electrolytes at Temperature up to 800°C and Pressure of 5 kbar Based on the Electrostatic Model, *Geokhimiya*, 1989, no. 3, p. 393.

9. Chudenko, K.V., Karpov, I.K., Bychinski, V.A., and Kulik, D.A., Current Status of the SELECTOR Software Package, *Proc. 8th Int. Symp. on Water–Rock Interaction*, Rotterdam, 1995, pp. 725–727.