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## HCh: New Potentialities for the Thermodynamic Simulation of Geochemical Systems Offered by Windows

Yu. V. Shvarov

*Geological Faculty, Moscow State University, Vorob'evy gory, Moscow, 119992 Russia*

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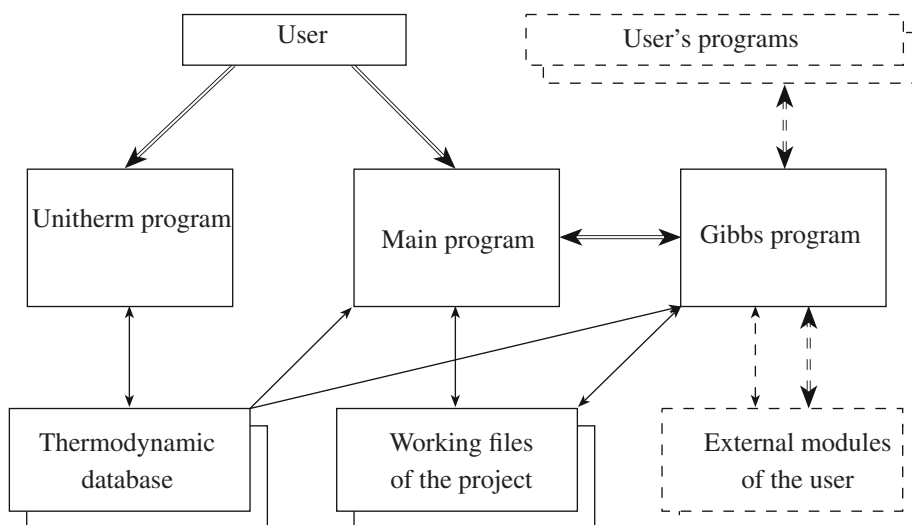
A need for the adequate physicochemical simulation of natural processes stimulates the constant development of modernization of simulation algorithms for the equilibrium compositions of chemical systems. Modern computer programs are able to simulate chemical equilibria in complex multicomponent heterogeneous systems, which include not only aqueous solutions and minerals of invariable composition but also solid solutions, alloys, gas mixtures, and nonaqueous liquid solutions and surface complexes. Currently available algorithms and computer programs underlain by the minimization of the thermodynamic potential of the system make it possible to solve problems of any complicacy and simulate numerous chemical processes of various nature occurring simultaneously in a given system. However, although the potentialities of the computer programs were significantly expanded during the past years and the programs themselves became much more accessible to researchers, the percentage of geochemical studies carried out by techniques of numerical simulations remains relatively low. This inconsistency seems to be explained largely by the fact that computer programs for physicochemical simulations were often developed for solving certain specialized problems and can hardly be adjusted for other, at least slightly different, geochemical systems or processes.

As a possible avenue for overcoming these difficulties, we proposed a simple method for the description of algorithms for physicochemical simulation, which was implemented in the HCh software package [1]. This approach makes use of a description of cyclic equilibrium simulations, which are created by the user in a specialized file of the *Control* type independently of the simulating program, and was proved highly efficient: the researcher can apply it to simulate his own models of geochemical processes that are not predetermined in the HCh package (see, for example, [2]). However, the application of this simple technique for the description of the simulation method ensures only the partial solution of the problem, because not every model can be described with it. For example, this

approach cannot be applied to formalize the solution process of some types of inverse geochemical and thermodynamic problems. This puts forth the problem of developing a program for the simulation of equilibrium with the possibility to completely specify the scheme and method of solution of the problems, although, of course, the means of this solution cannot be as simple as the language utilized in the description of dynamic models in *Control*.

Another factor hampering the application of the developed software in the simulation of a wider circle of geochemical problems is the diversity of the properties of natural phases, which cannot be described by a single or a small (and constant) number of thermodynamic models. In fact, any natural solution is nonideal, and, hence, there is no universally applicable model for nonideality that would provide a description of all specifics of their behavior under any possible conditions. Moreover, a general model for nonideality has not been developed even for aqueous solutions (the principal constituent of most geochemical processes), and this leads the researcher to utilize a certain program to model processes involving weakly mineralized solutions and another program to simulate processes with the participation of brines. If any geochemical system includes a phase whose nonideality model is not simulated by any program package, the modeling of such a system becomes impossible.

The aforementioned problems in expanding the applicability of thermodynamic simulation techniques in geochemistry can be overcome via a specialized design of the simulating program. For this purpose, the program for simulating the equilibrium compositions of a chemical system should allow for the possibility of incorporating the user's modules for the calculation of the activity coefficients for any solution (so-called "opening from bottom") and for addressing the program from outside, from a user's program, which is underlain by a different simulation algorithm (so-called "opening from top"). Both of these possibilities have already been implemented in the HCh package [1] but



**Fig. 1.** Interaction scheme of components of the HCh program package for Windows. Thin arrows correspond to information transfer, and double arrows show the transfer of control. Additional (user's) components are shown as dashed-line rectangles.

did not receive wide recognition ([3] is one of only a few positive examples) because of the low efficiency of the system of dynamic links between the programs in the DOS operation system. The situation became principally different when the HCh package was rewritten for Windows, in which dynamic links between programs is a basic architectural principle of the operation system.

#### DIFFERENCES BETWEEN THE PACKAGES FOR THE TWO PLATFORMS

The HCh package for Windows retains all potentialities of its DOS-based precursor and is fully compatible with it in terms of data. The latter fact means that, after switching to the Windows-based version, the user can immediately continue his simulations, using all of his accumulated files, including the Unitherm thermodynamic database. The new graphic interface of the package and the organizational principles of operations also remain as close as possible to those in the previous version in order to maximally simplify the transition to the new platform.

The newly developed version of the package has a number of advantages related to the operation system (for example, quantitative limitations imposed onto the available program memory were removed and the rate of calculations was increased) and the natural evolution of the utilized algorithms: the new version yields more precise and accurate calculation results and works more stably. A graphical interface, the multitasking character, and the integrated properties of the operation system made the work with the package more convenient and allowed the package itself to actively interact with other programs of the user. Below we will consider

only two, the most principal issues: the means of implementing the “transparency” (in the aforementioned sense) of the Gibbs program, which calculates the equilibrium state of the chemical system by minimizing its free energy.

Although the structure of the HCh package did not undergo any principal modifications with the transition to another platform, for the sake of clarity Fig. 1 reproduces (from [1]) the interaction scheme of the components of these packages and newly development potentialities, which are described below. It is pertinent to recall the purpose of the major components of HCh. The Unitherm program was devised to compile and process thermodynamic databases and works under the immediate control of the user. The simulation of geochemical systems and processes is carried out with the Main program, which makes it possible to create files necessary for the simulations (for example, files of the System type, which describe chemical systems, and files of the Control type, which describe the simulation algorithms) and process the simulation results. Equilibrium compositions are calculated by the Gibbs program, which is launched by the Main program; Gibbs utilizes files prepared by Main and the thermodynamic characteristics of compounds from the Unitherm database.

#### USER'S MODULES FOR CALCULATING ACTIVITY COEFFICIENTS

The Gibbs program is “open from bottom”, i.e., allows the user to create his own modules for calculating activity coefficients for any solution of the system and, when necessary, to make them available for the program in the course of calculations. It is important to

stress that the latter process does not require recompilation of any programs of the package and is controlled by a simple change in the input data: for this purpose, it is sufficient to list the names of the user's modules in a certain file and specify the corresponding solutions.

The Gibbs program makes use of the most efficient means of the incorporation of external modules for the calculation of activity coefficients via dynamic link libraries (DLL files). All of the user's modules have the format of usual DLL and the same logical structure but different names. If any solution of the modeled system requires another (i.e., not integrated in the Gibbs program) nonideality model, the user specifies the name of the library for this solution.<sup>1</sup> After the specified module is loaded into the computer memory, the work becomes undistinguishable (for the user) from that with the integrated modules of the Gibbs program.

Because the Gibbs program bears no a priori information on the algorithms in the user's modules, it calls all of them in a similar manner. For these accesses to be accurately processed, all modules have to have a similar logical structure, which is describe below.

The first entry point to the user's module is meant for the processing of the initial activation, when the Gibbs program transfers information on the solution (number of solute components, their names, and their chemical formulas, which will be processed by the module) to the module. The module can utilize this information for any preparatory routines (for example, memory allocation) if needed. The initial activation of each external module occurs only once, during the reading of the input data of the problem.

The Gibbs program accesses the user's modules through another entry point each time when external conditions (temperature and pressure) are changed in the system, i.e., when the standard potentials of the components of the system are calculated. Each module receives current values of the temperature, pressure, and the potentials of "its" components, because this information may be required for the module for its further operation. In addition, if the module changes the values of the received standard potentials (as can be needed for the algorithm implemented in the module), the Gibbs program will further use exactly those modified values.

The third entry point at the user's module is the main ("working"). The Gibbs program accesses through it the user's module each time when the algorithm for the calculation of equilibrium requires known activity

coefficients for a solution of specified composition: the module receives current values of the concentrations of components in the solution and sends the values of the activity coefficients back to the Gibbs program.

Finally, the fourth (final) entry point to each module enables the module to free the allocated memory and prepare for the unload operation. This type of access occurs only once before the termination of the problem solution.

The scheme described above for the interaction of the Gibbs program with external modules for the calculation of activity coefficients makes it possible to implement practically any algorithm in them for the calculation of the nonideality of a solution.

### ACCESS TO THE GIBBS PROGRAM FROM THE USER'S PROGRAMS<sup>2</sup>

The Gibbs program is "open form top", i.e., it can be utilized to calculate equilibrium compositions of a chemical system by accessing this program from a program developed by the user. This possibility (which also does not require recompilations of any programs of the HCh package) is readily available and easy to utilize because HCh makes use of the OLE Automation technology (designed by Microsoft). Hence, the user may implement any algorithm for equilibrium modeling if a programming environment supporting OLE is used. In addition to several widely applicable programming languages for Windows, this technology is also supported by such applications as MS Office, MATLAB, and some others.

In order to utilize all of these potentialities, the user first creates, using the HCh package tools, a file of the System type, which describes the chemical system in terms of components listed in the Unitherm thermodynamic database. After this, he creates, in his own program, a Gibbs object, which will further operate as an OLE server. The user calls the properties of the Gibbs object to specify its working parameters and methods for the purposes of the calculations.

**Main properties of the Gibbs object.** The two types of properties that must be specified from the user's program are as follows: (1) UnithermLocation, which specifies the pathway to the Unitherm working database (the computer's hard drive may contain many different Unitherm databases), and (2) SystemFile, which is the name of the file with the description of the chemical system. All other properties of the Gibbs object (for example, GibbsOptions, which specify the

<sup>1</sup> HCh currently has the following models for nonideality: the Debye-Hückel model (3rd approximation) for aqueous solutions [4], the Peng-Robinson (PRSV) model for mixtures of real gases [5], the Nonrandom Two Liquid (NRTL) model for liquid non-aqueous solutions [6], and a model for mixing of sites (MOS) for solid solutions [7].

<sup>2</sup> More detailed information about accessing the Gibbs program from the user's programs can be read in the documentation on the Gibbs program, which is available from <http://geol.msu.ru/deps/geochems/GibbsLib.doc>.



calculation regimes) are optional: if they are not specified, standard values are used.

**Main methods of the Gibbs object.** When the OLE technology is applied, the access to the method of the object is analogous to calling any usual calculation routine, as if it was contained in the user's program. To calculate an equilibrium composition, the following two methods can be utilized by the Gibbs object: CallGibbs and ReCallGibbs, which differ only in the sets of the parameters passed to them. The former method requires the whole initial input information on the calculated equilibrium to be specified: the temperature, pressure, potentials of perfectly mobile components, and the bulk (elemental) composition of the system and two arrays into which the object will send the equilibrium composition in terms of all dependent components and their chemical potentials. The other method carries out analogous calculations but requires fewer parameters and is usually applied in subsequent calculations, when some parameters of the system have already been specified in the course of previous accesses.

**Additional properties and methods of the Gibbs object.** Some properties of the modeled system may be determined or obtained without aforementioned calculation methods. For this purpose, the following (additional) properties and methods of the Gibbs object are designed: Libversion (returns the number of the Gibbs object version), SetFugacities (specifies the fugacities of the perfectly mobile components), GibbsExitWords (recovers the text describing the current state of the object), GibbsResult (recovers one specified value from the previously obtained equilibrium solution), and ShutDown (prepares the Gibbs object to be deleted in order to, for example, empty the memory).

**Specialized properties and methods of the Gibbs object.** The properties and methods of the Gibbs object listed above are sufficient to implement any algorithm for a direct or inverse problem of equilibrium geochemical simulations but are insufficient for the solution of some inverse thermodynamic problems. For instance, to determine the standard free energy values of a component from experimental data, their values should often be charged in the process of simulation (ignoring data from the Unitherm database). The following two methods of Gibbs objects are designed for the solution of inverse thermodynamic problems. The SetFreeEnergy method sets a free energy value specified by the user (or calculated by a program of the user) for a specified component of the system; this value will then be used in place of the standard one during all later accesses to calculation techniques until this option is canceled. The other method is SetBinParm, which makes it possible to change the values of any parameters in a user's program for the binary interaction in the NRTL (Nonrandom Two-Liquid) and PRSV (Peng–Robinson–Stryjek–Vera) nonideality models integrated in HCh; this option

makes it possible to optimize parameters of the binary interaction in these models based on the results of equilibrium experiments in gas and liquid (nonaqueous) solutions.

#### EXAMPLE: BINARY ALBITE–ANORTHITE SOLID SOLUTION

Let us explore in much detail the Holland and Powell model for the calculation of equilibrium with plagioclase before utilizing this model. For this purpose, we write an external *Ab\_An.dll* module, which calculates the activity coefficients of albite and anorthite in their binary solution by formulas from [8], and connect this module to the Gibbs program. Using the Main program, we have to create a file of the System type, which describes the system consisting of a single albite–anorthite binary solution.

Let us insert a macros (written in the VBA language) into an Excel workbook, with this macros creating a Gibbs object and invoking necessary methods for this object to calculate equilibria in our system throughout its whole compositional range with a step of 0.01 of mole fraction units. The calculation results yielded by this Gibbs object are the chemical potentials of the end members and their activities. Let us select the latter and use the Excel tools to immediately graphically represent the results received from Gibbs. Figure 2 shows the values of the albite and anorthite activities in their binary solution that were calculated by this method at a temperature of 100°C. As can be seen from the plot, the solubility of both components under these conditions is characterized by significant nonideality at low concentrations.

The plot also exhibits the limited mutual solubility of the end members under these conditions and implies that the solid solution should undergo breakdown. To simulate this process, we should modify the file for the description of the chemical system with allowance for *two identical plagioclases* in it.

After the aforementioned modification of the System file, we will also modify our Excel macros: now it will calculate the free energy of one of the plagioclases and the system as a whole. The plot thus obtained (for the same temperature) is shown in Fig. 3. The thin line in it is the reduced free energy of mixing for albite and anorthite. Inasmuch as this line is not convex, the solid solution should decompose. Because the file with the description of the system contains two identical plagioclases, the Gibbs program obtains two solid solutions in the equilibrium state in the middle segment of the plot: an albite-rich and anorthite-rich solution. The total reduced energy of the system calculated by the program is shown in the diagram with a heavy line.

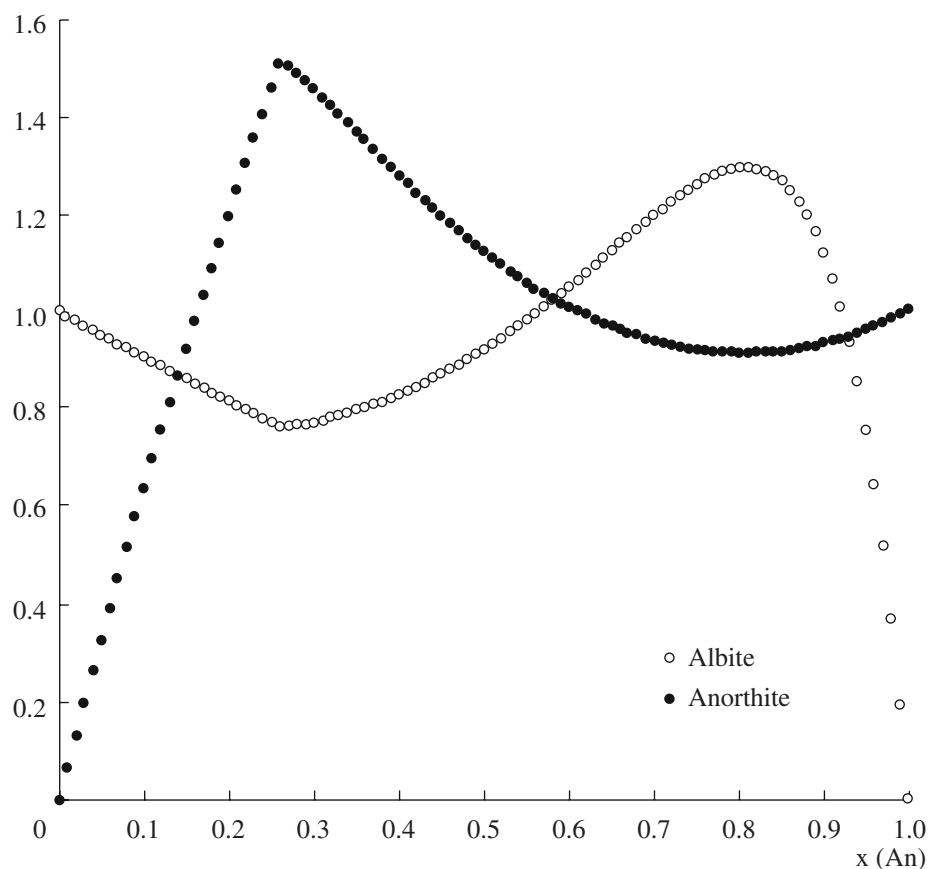


Fig. 2. Albite and anorthite activities in the binary plagioclase solid solution (calculated according to [8],  $T = 100^\circ\text{C}$ ).

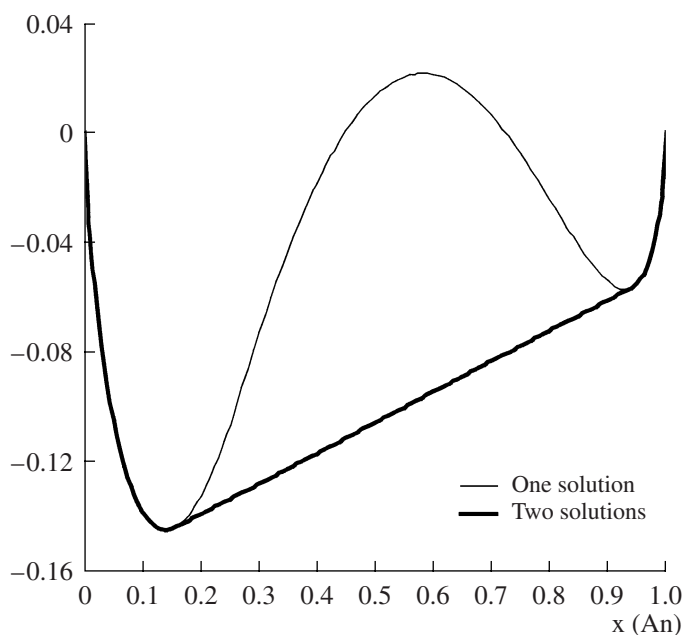


Fig. 3. Reduced energy of mixing ( $G_{\text{mix}}/RT$ ) for the albite-anorthite binary solid solution (calculated according to [8],  $T = 100^\circ\text{C}$ ). The thin line is the solid solution energy, and the heavy line is the energy of the system with regard for the breakdown of the solid solution.

## CONCLUSIONS

The applicability of thermodynamic simulation techniques in the study of geochemical systems and processes may be quickly and efficiently expanded if the architecture of the programs for the calculation of chemical equilibria allows the user himself to increase its capabilities when required. This publication represents two techniques for the solution of this problem. One of these methods (“opening the program from bottom”) enables the user to specify (program) a model for the nonideality of the real solutions and dynamically incorporate them into the modeling program. The other technique (“opening of the program from top”) makes use of the OLE Automation technology, which makes it possible to access the program for the calculation of the equilibrium compositions of complex systems from a program written by the user. This architecture is implemented in the Gibbs program in the HCh package for Windows, and the example presented above demonstrates that abilities can be used simultaneously.

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