GEOCHEQ – THE COMPLEX FOR THERMODYNAMIC MODELING OF GEOCHEMICAL SYSTEMS

M.V.Mironenko, N.N.Akinfiev*, T.Yu.Melikhova*
Vernadsky institute of geochemistry and analytical chemistry, RAS, Moscow
***** Moscow state geological prospecting academy, Minvuz, Moscow

This study was supported by the Russian Fundamental Research Foundation (Project No. 99-05-65545)
Herald DGGGMS RAS № 5 (15)'2000 v.2
URL: *http://www.scgis.ru/russian/cp1251/h_dgggms/5-2000/term10.eng*

A complex is under development in Windows media for thermodynamic modeling. It consists of a database of thermodynamic data and a code to calculate chemical equilibria in multicomponent nonideal systems. The paper describes the current state and abilities of the complex as well as plans of it's further development.

The program complex ***GEOCHEQ*** consists of the four blocks: 1) a thermodynamic data base and programs to work with it; 2) a block for calculating thermodynamic properties of the components; 3) a block for computation of a chemical equilibrium of the system; 4) routines of calculating activity coefficients of species of the gas and aqueous solutions.

1. Thermodynamic database is based on the well known package SUPCRT92[1] and permits corrections and additions of a user. In particular the data base has been completed with data of [2,3,4], which have been consisted with SUPCRT92. These data use the same formats of the data as HKF [5]. Thus now the database ***GEOCHEQ*** contains 194 minerals, 18 gases, and 954 aqueous species.

The special routines of the database permit to choose independent components (chemical elements) of a task; they select automatically the components from the database that are compatible with specified independent components; permit further selection of the components to be deleted, specifying temperature and pressure. These routines have been realized in **MICROSOFT ACCESS** media under **WINDOWS 95**.

2. ***Calculation of thermodynamic properties of the components*** for specified temperature and pressure is carried out **for water** – with the fundamental multiparametric equation of Hill[5]. Calculation of electrostatic properties of H_2O is carried out with the equation of Archer and Wang[6]; for minerals and pure gases – with the three member equation of Miyer-Kelly. There is a possibility to take into account the phase transitions of minerals at elevated temperatures and pressures. For this goal in the database the corresponding positions have been foreseen for the minerals with 2 and 3 etc. phase transitions and corresponding calculating utilities have been developed. Thermodynamic properties of **aqueous species (ions and neutral species)** are calculated with the equation of state of Helgeson-Kirkham-Flowers (HKF) [4]. This equation permits to calculate standard thermodynamic properties within the wide range of temperatures (0 – 1000°C) and pressures (1 – 6000 bar).

3. ***Calculating equilibrium compositions of systems.*** The program code ***CHEMEQ*** has been developed to calculate equilibria in closed systems using the Gibbs energy minimization method. The algorithm of convex simplex has been realized [7].

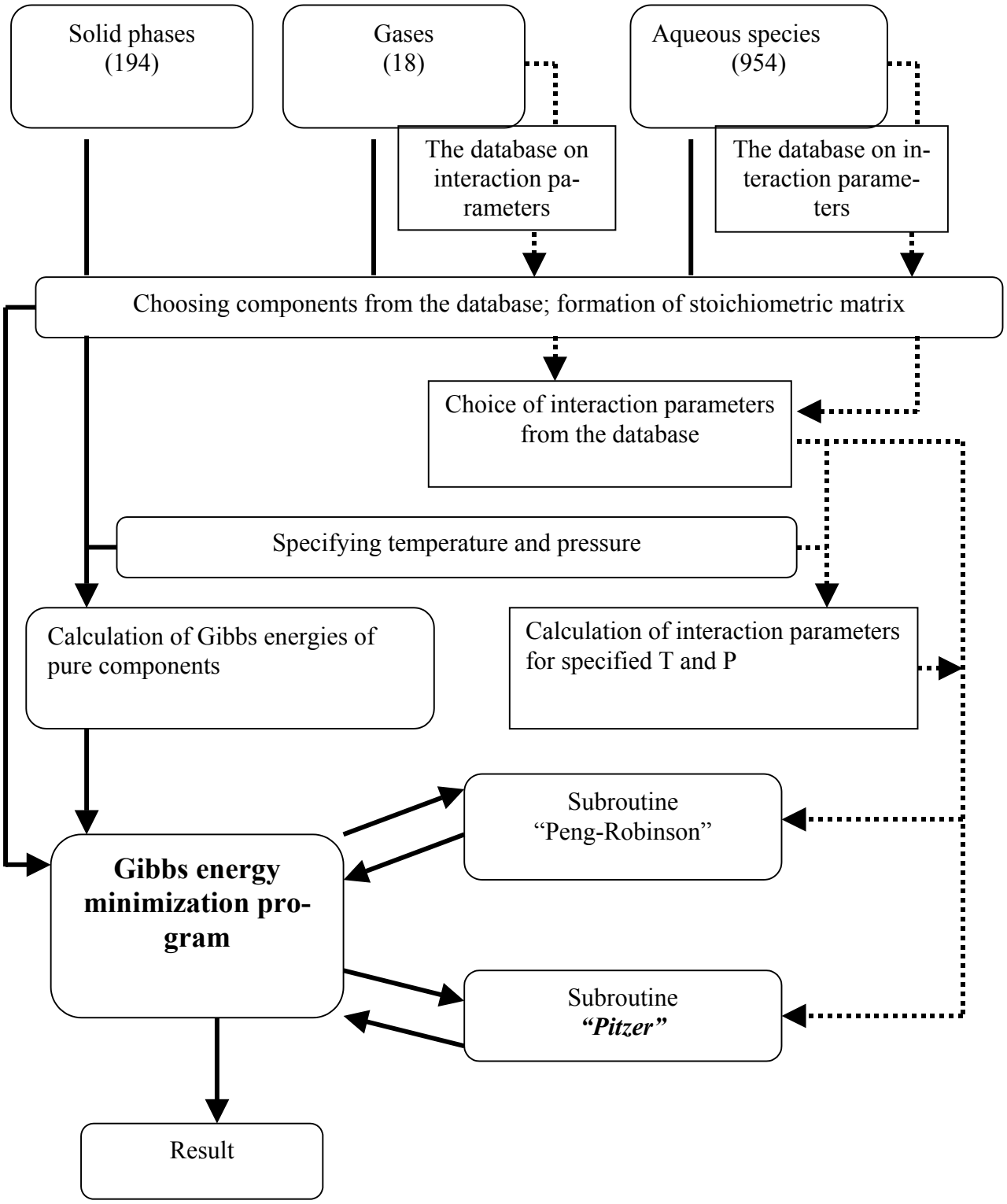
4. ***Calculation of activity coefficients*** is carried out with Pitzer model or Debye-Hückel model for aqueous solutions and with Peng-Robinson equation for gas solutions.

Current state of the model permits to calculate chemical equilibria in the systems that consist of one component solids and/or an aqueous solution (Debye-Hückel model), and/or an ideal gas phase.

The diagram shows an interaction of the blocks of the database with calculating modules. The gray blocks haave been already developed, the another blocks are under development. The currently untied blocks are connected with dashed lines.

1. *Shock E.L., Sassani D.C., Willis M., Sverjensky D.A.* Inorganic species in geologic fluids: Correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complexes // Geochim. Cosmochim. Acta, 1997. V. 61. P. 907-950.
2. *Akinfiev N.N., Zotov A.V.* Thermodynamic description of chloride, hydrosulfade, and hydroxide complexes of Ag(I), Cu(I) и Au(I) at 25 – 500°C and 1 – 2000 bar // Geochemistry, 2000, In press.
3. *Tanger IV J.C., Helgeson H.C.* Calculation of the 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. // Amer. J. Sci., 1988. V.288. P. 19-98,
4. *Hill P.G.* A unified fundamental equation for the thermodynamic properties of H_2O // J. Phys. Chem. Ref. Data, 1990. V. 19. P. 1233-1274.
5. *Archer D.G., Wang* . The dielectric constant of water and Debye-Hückel limiting law slopes // J. Phys. Chem. Ref. Data, 1990. V. 19. P. 371-411.
6. *de Capitani C. and T.H. Brown* The computation of chemical equilibrium in complex systems containing non-ideal solutions.//Geochim. Cosmochim. Acta, 1987. V. 51. P. 2639-2152.
7. *Kestin J., J.V.Sengers, B.Kamgar-Parsi, J.M.H.Levelt Sengers* Thermophysical Properties of Fluid H_2O // J.Phys.Chem.Ref.Data, 1984, v.13, No.1, 175-183.
8. *Johnson J.W., Oelkers E.H., and Helgeson H.C.* SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bars and 0^o to 1000^oC // Comp. Geosci., 1992. V. 18. P. 899-947. Peng D.Y. and Robinson D.B. // Ind. Eng. Chem. Fundam., 1976. V.15 P.90.
9. *Shock E.L., Helgeson H.C., Sverjensky D.A.* Calculation of the thermodynamic properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species // Geochim. Cosmochim. Acta, 1989. V. 53. P. 2157-2183.

Thermodynamic database



Interaction of the modules of the thermodynamic database and the calculating modules of the model

Completed modules

Not completed modules

Acting connections between modules

The connections must be established