

Methods and experimental techniques

#Dorogokupets P.I. Equation of state for minerals based on the method of potentials in the Bose-Einstein approximation

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Thermodynamic calculations in the Earth mantle conditions requires a knowledge of internally self-consistent functions for minerals at high temperatures and pressures. This problem is solved using the well-known method of potentials in the Debye approach [1-6]. Other approaches to the problem are also known [7-10]. Otherwise, diverse simplifications would be admitted for calculation of thermodynamic functions, as it was proposed in [11].

The main purpose of the present study is to modify the formalism assumed in [1]. Instead of the used Debye function, we approximate the thermal part of the Helmholtz energy by the Bose-Einstein function. This function was proposed in [12] for description of the Gibbs energy at zero pressure, but it is useful enough for the approximation of the Helmholtz energy, i.e. for VT realtions. As a result, we obtain a series of equations for presentation of thermodynamic functions of volume and temperature. We can apply this series of equations for calculation of any thermodynamic functions, if we previously find fitting parameters for a model, which optimize the available experimental measurements of heat capacity and relative enthalpy in dependence on T , volume as a function of temperature and pressure, coefficients of thermal expansion, bulk moduli, etc. Thus, we obtained a simple thermodynamic equation of state for mantle minerals, which allowed both to evaluate a self-consistent database of any thermodynamic functions by using experimental data, and their calculation in the wide intervals of T and P . The equation is also applicable for the construction of petrological and geophysical model for the Earth interiors.

Consider the Helmholtz free energy $F(V, T)$ as a sum [1, 13]:

$$F(V, T) = U_0 + E_p(V) + F_{th}(V, T) + F_a(V), \quad (1)$$

where U_0 – initial energy at 0K, $E_p(V)$ – the potential portion of the free energy, which depends only on volume, $F_{th}(V, T)$ – the thermal portion of the free energy, which depends on volume and temperature, $F_a(V)$ – the anharmonic portion of the free energy, which depends on V .

The potential portion of the free energy we take as [14]:

$$E_p = \frac{1}{2} K_0 V_0 [(\ln x)^2 - \frac{K'-2}{3} (\ln x)^3], \quad (2)$$

where K_0 and V_0 are bulk modulus and volume at zero temperature and pressure, $K' = dK_0/dP$, $x = V/V_0$. The

The model was tested using magnesite and periclase. This study was supported by the Russian Foundation for Basic Research, grant № 99-05-64891.

pressure $P(V) = -\partial E_p / \partial V$ and bulk modulus $K_T(V) = -V(\partial P(V) / \partial V)$ written as:

$$P(V) = K_0 \frac{1}{x} [-\ln x + \frac{K'-2}{2} (\ln x)^2], \quad (3)$$

$$K_T(V) = K_0 \frac{1}{x} [1 + (1-K') \ln x + \frac{K'-2}{2} (\ln x)^2], \quad (4)$$

The thermal portion of the free energy can be defined in the Bose-Einstein approximation:

$$F_{th} = m_B RT \left[\frac{\Theta_B}{2T} - \ln(1+b) \right] + m_{E1} RT \left[\frac{\Theta_{E1}}{2T} + \ln \left(1 - \frac{1}{\exp(\Theta_{E1}/T)} \right) \right] + m_{E2} RT \left[\frac{\Theta_{E2}}{2T} + \ln \left(1 - \frac{1}{\exp(\Theta_{E2}/T)} \right) \right], \quad (5)$$

where R – gas constant, m_B, m_{E1}, m_{E2} – degrees of freedom of each contribution, and $m_B + m_{E1} + m_{E2} \geq 3n$, where n is equal to the number of atoms in a unit cell; $\Theta_B, \Theta_{E1}, \Theta_{E2}$ – characteristic temperatures of the Bose and two Einstein contributions, $b = 1/[\exp(g)-1]$, $g = d \ln[1 + \Theta_B/(Td)]$, d – the power parameter, regulating behavior of heat capacity near 0K. A linear dependence of heat capacity on temperature can be obtained at $d = 1$, this dependence is close to the Debye heat capacity at $d = 4$, and it reaches the Einstein heat capacity at large d .

Using (5), the dependence of an internal energy and isochoric heat capacity in dependence on temperature at constant volume could be evaluated:

$$E_{th} = m_B R \left(\frac{\Theta_B}{2} + \frac{\Theta_B T d b}{T d + \Theta_B} \right) + m_{E1} R \left[\frac{\Theta_{E1}}{2} + \frac{1}{\exp(\Theta_{E1}/T) - 1} \right] + m_{E2} R \left[\frac{\Theta_{E2}}{2} + \frac{1}{\exp(\Theta_{E2}/T) - 1} \right], \quad (6)$$

$$C_{Vth} = m_B R \left(\frac{\Theta_B d}{T d + \Theta_B} \right)^2 b(1/d+1+b) + m_{E1} R \left(\frac{\Theta_{E1}}{T} \right)^2 \frac{\exp(\Theta_{E1}/T)}{[\exp(\Theta_{E1}/T) - 1]^2} + m_{E2} R \left(\frac{\Theta_{E2}}{T} \right)^2 \frac{\exp(\Theta_{E2}/T)}{[\exp(\Theta_{E2}/T) - 1]^2}, \quad (7)$$

A thermal pressure could be evaluated from (5) by differentiation of the free energy with respect to volume at constant temperature $P_{th} = -(\delta F_{th} / \delta V)_T$:

$$P_{th} = \tilde{\alpha}_B E_B / V + \tilde{\alpha}_{E1} E_{E1} / V + \tilde{\alpha}_{E2} E_{E2} / V, \quad (8)$$

where E_B, E_{E1}, E_{E2} are the Bose and Einstein contribution to the internal energy in correspondence with (6), $\gamma_B, \gamma_{E1}, \gamma_{E2}$ – the Gruneisen parameters, which correspond to logarithmic derivatives $\gamma = -(\delta \ln \Theta / \delta \ln V)_T$ of each contribution.

The isothermal bulk modulus can be inferred from the thermal pressure $K_{th} = (\delta \ln P_{th} / \delta \ln V)_T$

$$K_{Th} = P_{thB}(1 + \gamma_B + q_B) - \gamma_B^2 TC_{VB} / V + P_{thE1}(1 + \gamma_{E1} + q_{E1}) - \gamma_{E1}^2 TC_{VE1} / V + P_{thE2}(1 + \gamma_{E2} + q_{E2}) - \gamma_{E2}^2 TC_{VE2} / V, \quad (9)$$

where P_{thB}, P_{thE1} and $P_{thE2}, C_{VB}, C_{VE1},$ and C_{VE2} are the Bose and Einstein contributions to the thermal pressure and isochoric heat capacity, $q_B, q_{E1},$ and q_{E2} are logarithmic derivatives $q = (\delta \ln \gamma / \delta \ln V)_T$. Above the Debye temperature, the anharmonic effects become notable in heat capacity. These effects should be added into our

model. Following to [1], the anharmonic portion of the free energy can be written:

$$F_a(V) = -a(V)T^2, \quad (10)$$

where $a(V)$ is the anharmonic parameter.

Subsequently we obtain

$$E_a = aT^2, \quad S_a = 2aT \quad \text{и} \quad C_{Va} = 2aT, \quad P_a = \gamma_a E_a / V, \quad \gamma_a = (\partial \ln a / \partial \ln V)_T, \quad K_{Ta} = P_a(1 - \gamma_a) \quad (11)$$

In this equation, γ_a does not depend on volume.

Differentiating pressure with respect to temperature at constant volume, we deduce an isothermal slope:

$$(\partial P / \partial T)_V = \gamma_B C_{VB} / V + \gamma_{E2} C_{VE1} / V + \gamma_{E2} C_{VE2} / V + \gamma_a C_{Va} / V \quad (12)$$

and, further, we calculate the coefficient of thermal expansion $\alpha = (\delta P / \delta \ln T)_V / K_T$.

Consider the dependence of the Gruneisen parameter and the characteristic temperature on volume in the classic expression:

$$\gamma = \gamma_0 x^q \quad \text{и} \quad \Theta = \Theta_0 \exp[\gamma_0(1 - x^q)/q] \quad (13).$$

Enthalpy and Gibbs energy can be evaluated from the relations $H = E + PV$, $G = F + PV$.

Finally, forming the system of equations, we demand the Gruneisen parameter to correspond to thermodynamic relations at all conditions, i.e.

$$\gamma = \alpha K_T V / C_V, \quad \gamma = \alpha K_S V / C_P,$$

where K_S – an adiabatic bulk modulus, C_P – heat capacity at constant pressure.

The proposed model allows to calculate any thermodynamic functions at given temperature and volume, using known fitting parameters (U_0 , V_0 , K_0 , K' , d , m_B , m_{E1} , m_{E2} , Θ_B , Θ_{E10} , Θ_{E20} , a_0 , γ_B , γ_{E10} , γ_{E20} , γ_a , q_B , q_{E1} , q_{E2}). They can be obtained using the least square method by experimental measurements of heat capacity, enthalpy, volume, coefficient of thermal expansion, bulk moduli, and other data. The model can be significantly simplified, suggesting that the Gruneisen parameter and q are similar for all thermal portions. In this case, we have the following fitting parameters: (U_0 , V_0 , K_0 , K' , d , m_B , m_{E1} , m_{E2} , Θ_B , Θ_{E10} , Θ_{E20} , a , γ , γ_a , q).

The model was tested by examples of magnetite and brucite.

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#Morgunov K.G., Kolonin G.R., Shironosova G.P. The "REETHERM" data base for modeling of geochemical processes with participation of rare-earth elements.

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key words [database REE dissolved forms complexation hydrothermal solutions thermodynamic modeling]

The development of the data base (DB) of thermodynamic properties of minerals and aqueous species [1,2,etc.] gives a chance for physico-chemical modeling of the reasons and directions of REE and Y fractionation in the processes of hydrothermal ore-formation with the use of thermodynamic methods. The authors' experience suggests that the following well-known data base like the data bases included into the "Selector" program computing complex [3], the "UNITHERM" data base created for the "GIBBS" program of minimization of free energy [4], presently included into the Hch program complex [5], SUPCRT92 [6], SUPCRT96 [1], etc. are the suitable basis to solve this problem. The authors have created the

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"REETHERM" data base, which uses the HKF equation as the main algorithm to provide possibilities for modeling hydrothermal equilibria with participation of REE. The use of the Delphi Client/Server program language and the presentation of information in the files of the dBase format makes it possible to use the base for the work with information networks. The developed software is intended for use in the Windows operation system. The proposed base of thermodynamic information consists of the following three connected data bases: BASE1, BASE2 and BASE3. The structure of their files is shown in Fig.1.

Fig.2 gives an arrangement of the program algorithm, the work of which consists of the following stages: 1) selection of the data of chemical formula of a required compound from the list in BASE1;

2) search for the required compound in the SPECIES field of the data base of HKF parameters with the help of SEARCH1 subprogram; 3) search for the reaction of the required compound in SPECIES field, connecting BASE1 and BASE2, with the help of SEARCH2 subprogram; 4) the execution of the operation to select from the equation of the reaction of complex formation of chemical formulae of all the particles, participating in the reaction and their corresponding stoichiometric coefficients by DISTINGUISH subprogram; 5) search for the components of the reaction on SPECIES field in the database of HKF parameters, using SEARCH3 subprogram; 6) creation of the file of initial data and corresponding BASE3 bibliographic data of REFERENCE field; 7) computing and displaying the final result as the logarithms of stability constants of the given complex in the whole range of temperatures and pressures.

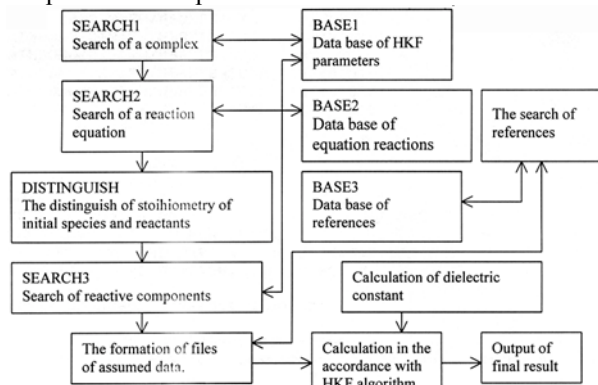


Fig. The general scheme of the used software.

In the present stage of "REETHERM" data base formation the main attention is paid to hydroxyl, fluoride, carbonate and bicarbonate complexes of REE, which play the main role in geochemical processes with participation of lanthanides. Moreover (In this case), the special program provides the means for the correction of constants for two latter types of complexes in the context of changing the dielectric permeability of the solvent with elevated contents of carbon dioxide as a nonpolar gas component [7].

The potential users can obtain an extended information on "REETHERM" data base and the possibility to use its data on the web-site

(<http://www.uiggm.nsc.ru:8082/uiggm/mineralogy/lab454/program.htm>) of the site of the United Institute of Geology, Geophysics and Mineralogy, SB RAS.

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#Slutskiy A.B. Pressure calibration of the piston-cylinder apparatus in the region of relatively low pressures, 4-20 kbar.

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The piston-cylinder apparatus with solid pressure-transmitting media are usually used for generation of pressure of above 20 kbar. It relates to friction losses, which become comparable to pressure values at lower pressures. Using the media with a low coefficient of friction loss allows to broaden the region of the apparatus application to lower pressure, right up to the pressures of several kbars. In this case, the problem of pressure estimation in a camera remains, i.e. how much the real pressure differs from its calculated value, which can be defined as a ratio of compression to the piston area. In order to calibrate the camera within the region of 4-16 kbar, an influence of pressure on the melting temperature of KCl was studied. The influence of pressure on the melting temperature of salt was investigated in the cycle of compression and decompression using the apparatus equipped with the 3/4-inch camera. Temperature of KCl melting was measured by the method of the differential thermal analysis (DTA). The obtained hysteresis loop defines a double value of friction losses, $2\Delta P$. A width of the hysteresis loop increases with pressure because of an increase of friction losses. The double value of friction losses allows to precisely estimate pressure in the camera. Assuming that the friction losses during compression and decompression are of similar value, we obtain, that the real curve of dependence of the KCl melting temperature on pressure occurs in the middle of the hysteresis loop. The pressure losses at the expense of frictions, calculated for our camera, are 0.5-1 kbar for the salt cell used. An accuracy of pressure determination in the camera is related to an error of estimation of friction losses, which, in turn, depend on an error of determination of the melting temperature on the thermogram (about 3°C). Taking into

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account a good consistency of measurements and the error of melting temperature, we obtain a total error of pressure determination as 3-4 %. Our data, obtained by the DTA method in quasi-hydrostatic conditions using a salt as a pressure-transmitting media, are in a good agreement with the results of determination of the dependence of the KCl melting temperature on pressure in hydrostatic conditions.

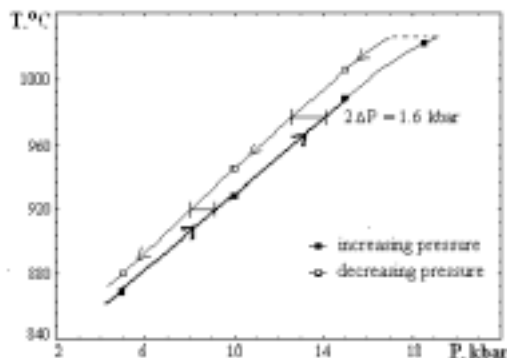


Fig.1. Curves of KCl melting in the cycle of compression and decompression.

Kolesov G.M., Shubina N.A., Lyul' A.Yu. Application of optimized neutron-activation analysis for assessment of chemical composition of extraterrestrial samples

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key words [*meteorites, lunar rocks, space dust, instrumental neutron activation analysis, conditions of the analysis, optimisation*]

The chemical composition is the determining characteristics of any objects and, especially, such unique ones as meteorites, chondrules, refractory inclusions, lunar rocks and space dust. These objects are presented usually in a small quantity for the lab investigations. Therefore the methods used should be highly efficient. We used the INAA [1].

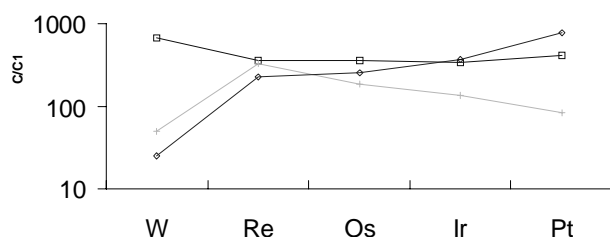


Fig. Three types of distribution of refractory siderophilic elements in fragments of chondrite Kainsaz testify that these inclusions formed in different processes and oxidative-reductive conditions in the protoplanetary disk.

A method of numerical modelling of gamma-spectra of any given composition using experimental data on isotopic spectra of individual elements (irradiated with reactor neutrons) and software comprising all steps of instrumental neutron activation analysis were developed for effective assessment of chemical composition of extraterrestrial samples. The signal-to-noise ratio (Fk) for gamma-ray lines in a complex gamma-spectrum formed

by the mixture of radioisotopes of an element in the test sample was taken as a criterion for optimization. The samples were irradiated with reactor neutrons (flux is $8.6 \cdot 10^{17} \text{ n/cm}^2$).

The calculation of optimal conditions of analysis and irradiated spectra processing were carried out by the software written in FORTRAN 5.0. It includes 6 successive programs as follows [2]: **1.** Search for analytical peaks and evaluation of Compton background in the experimental spectra of individual elements. The background is evaluated from the left to the gamma-line with the most value of energy in the individual element spectrum. From the right the background is assumed to be zero. The files of Compton background in gamma-spectra of individual elements and integrated file of the peak areas without background for all considered spectra are created as a result of the program work. **2.** Normalisation of the peak areas and their background values (to 1 hour of irradiation, 1 μg of mass, 1 hour of cooling). Thus the calculation of impulse numbers in spectra for identical conditions of their formation is performed. **3.** Transposition of the Compton background matrix. As a result the two-dimensional matrix of radionuclides is formed and every its value on horizontal line agrees with a contribution of every constituent element in Compton background of the studied line. **4.** Calculation of the limiting permissible values of the analysis conditions at which the total number of impulses per second from irradiated sample should not exceed the given value, i.e. the program calculates the permissible values of loading for measuring equipments. **5.** Determination of a possibility to detect the peak in the given matrix within the limits of permissible values of analysis conditions and the maximal signal-to-noise ratio in the mentioned limits and thus determining the optimal irradiation, decay, counting times. **6.** Creation of the final table for more than 100 gamma-lines of radionuclides considered. It includes the feasibility of an element determination using the respective gamma-line in the given conditions, the cooling time when a given gamma-line is detected, the maximal signal-to-noise ratio and corresponding cooling time, possible interference of the gamma-lines and cooling time when interference absent.

The method was tested by the analysis of reference materials such as effusive (ST-1A) and intrusive (SGD-1A) basite and stone (Allende) and iron (Sikhote-Alin') meteorites. The matrix effects were minimized, the interference of lines was decreased and the number of determinable elements was increased up to 40. The decrease were made for the detection limits ($10^{-4} - 10^{-8}$)% and analysis errors (5-15)% too.

Also NAA was used for searching and distinguishing fragments with ultrarefractory inclusions (with extremely high concentrations of Ir, Os, Sc, Pt) from carbonaceous chondrites (Kaisaz (Fig.), Efremovka, Allende), chondrules, various spherules etc.

The method can be applied for studying some other global processes of matter evolution in the Solar system.

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#Vigasina M.F., Orlov R.Yu. The determination of thermodynamic potentials of substances by ab-initio calculations.

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The quantum-chemical calculations of the thermodynamic properties of substances are at present quite useful for studying chemical reactions.

In opposite to the conventional thermodynamic scale of energy there is a common zero level of energy for all substances for the ab-initio calculations. It is such a state of the system when all electrons and nuclei are separated from each other to the infinity. The energy equilibrium of the reaction takes into account the rebuilding of the external atomic and molecular orbitals of all molecules and atoms participating in the reaction. Besides the thermodynamic potentials it maintains the energy E of all electron-nuclear interactions. Taking into account the full energy, the enthalpy of formation of any substance may be expressed as:

$$\Delta H_f = \Sigma(E+H)_{fin} + \Sigma(E+H)_{init} \quad (1).$$

The enthalpy of formation of some gaseous compounds can be established in the usual conventional thermodynamic scale if the quantum-chemical calculations of the full energy (E+H) of all initial simple related substances forming this compound is possible. In this case one has $\Delta H_f = \Delta H_r$.

The study of the enthalpy of formation of some mercury complexes accomplished by J. Tossell [1] is a good illustration of this possibilities. In his study the difference between the experimental and calculated data is only 1÷10 kcal/mol. It must be mentioned that the value of the items in equation (1) is nearly 10^5 kcal/mol.

The great difficulties arise when some simple substances in the reaction are crystals, for example C, W and others. The full energy of the crystal is the sum of its atomisation energy and the energy of atoms themselves. These calculations are not the routine procedure. But if one considers the reaction with the known value of ΔH_r and with the only one crystalline matter, its full energy can be determined by means of calculating the full energies of the other simple substances of the reaction:

$$(E+H)_{cryst} = \Sigma(E+H)_{fin} - \Sigma(E+H)_{init-1} - \Delta H_r.$$

The crystal full energy obtained in such a way can be used for the calculation of other reactions with the participation of this crystalline substance. For example, one may consider the reaction $C_{graphite} + O_2 = CO_2$ with the known enthalpy $\Delta H_r^{298.15} = -94,1$ kcal/mol [2]. In accordance to quantum-chemical calculation $(E+H^{298.15})_{CO_2} = -117774$ kcal/mol, $(E+H^{298.15})_{O_2} = -93904$ kcal/mol. Then the full energy of the crystalline

graphite is $(E+H^{298.15})_{graphite} = (-117774 + 93904 + 94)$ kcal/mol = -23776 kcal/mol.

In this way the reactions of formation $C_2, C_3, C_5, CO, CO_2, C_2O, CH, CH_2, CH_4$ and CH_3 participating graphite were studied. Finally, the mean value of the full energy of graphite was $(E+H^{298.15})_{graphite} = -(23780 \pm 13)$ kcal/mol.

In a same manner the energy of a crystalline tungsten $(E^*+H^{298.15})$ was calculated using the reaction $W_{cryst} + 2O_2 + H_2 = H_2WO_4$, the known value $\Delta H_f^{298.15} = -216.707$ kcal/mol [3] and the effective core potential SBK [4] for tungsten. Ab initio calculation gives $(E+H^{298.15})_{H_2} = -696$ kcal/mol, $(E+H^{298.15})_{O_2} = -93904$ kcal/mol and $(E^*+H^{298.15})_{H_2WO_4} = -230830$ kcal/mol. Consequently the SBK-energy of tungsten $(E^*+H^{298.15})_W = -42109$ kcal/mol.

This result was applied to the calculation of the unknown thermodynamic properties of gas WF_4 described by the reaction $W_{cr} + 2F_2 = WF_4$. It was obtained for the free molecule WF_4 : $\Delta H_f^{298.15} = -317$ kcal/mol in the conventional thermodynamic scale. Consuming the value of entropy calculated for WF_4 in this study ($S^{298.15} = 83$ cal/mol·K) and published data for W_{cryst} (7.81 cal/mol·K [2]) and F_2 (48.51 cal/mol·K [2]) we obtained for WF_4 : $\Delta S_f^{298.15} = 27$ cal/mol·K. Consequently the Gibbs free energy of formation of WF_4 is $\Delta G_f^{298.15} = -325$ kcal/mol.

Our calculations were made at the restricted Hartree-Fock level by means of quantum-chemical GAMESS computer programs. The equilibrium structures were calculated at the base electron state. For tungsten we used SBK effective core potential. The atoms of oxygen, chlorine and hydrogen were calculated with the triple zeta valence basis sets with the adjusted polarization orbitals of d-type at oxygen and chlorine and p-type at hydrogen.

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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

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describes the current state and abilities of the complex as well as plans of its further development.

The program complex **GEOCHEQ** consists of the four blocks: 1) a thermodynamic database 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 database has been completed with data of [2,3,4], which are consistent with SUPCRT92. The same formats of the data as HKF [5] is used. 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 H₂O is carried out with the equation of Archer and Wang[6]; for minerals and pure gases – with the three member equation of Miya-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

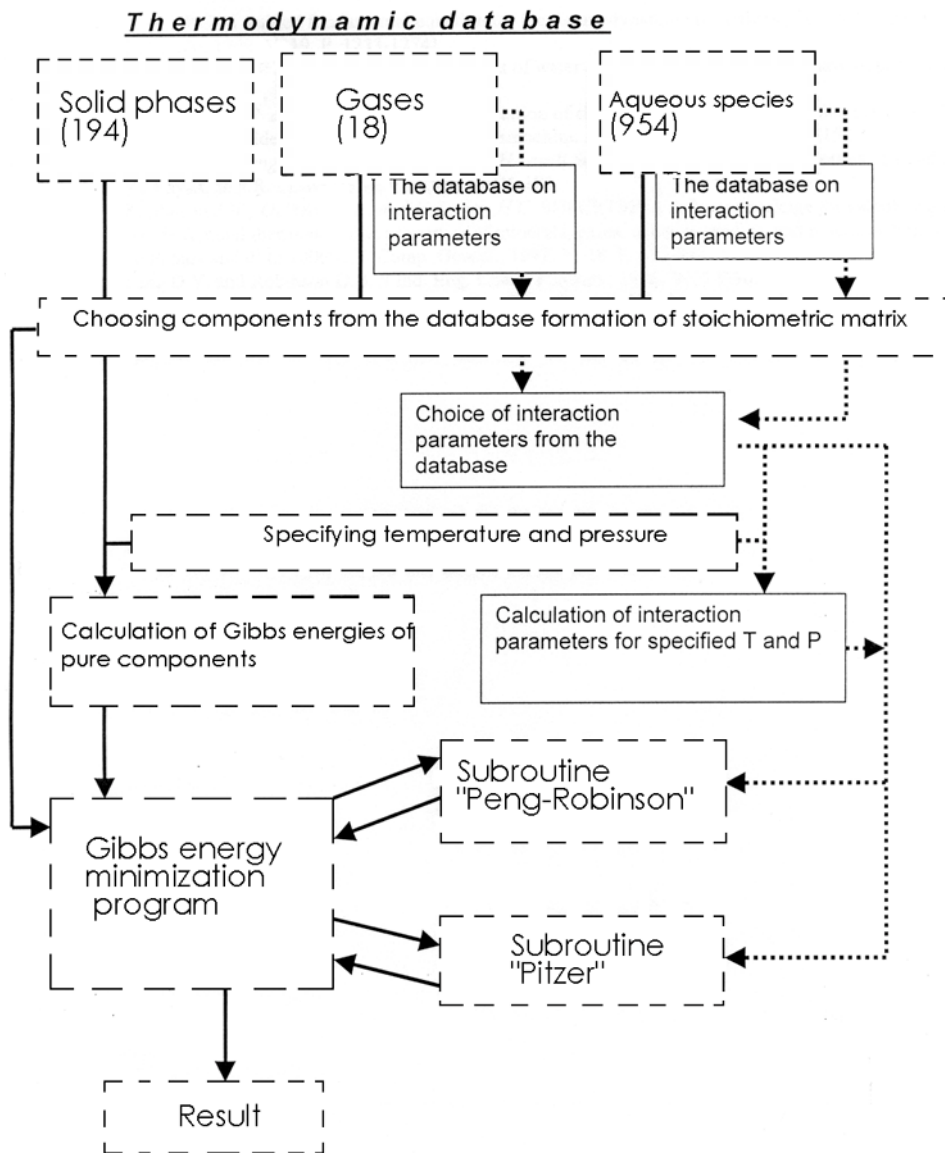
component solids and/or an aqueous solution (Debye-Hückel model), and/or an ideal gas phase.

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

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

Completed modules Acting connections between modules \rightarrow

Not completed modules The connections must be established $\cdots\rightarrow$