ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2010, Vol. 84, No. 5, pp. 728–734. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © K.G. Morgunov, 2010, published in Zhurnal Fizicheskoi Khimii, 2010, Vol. 84, No. 5, pp. 824–831.

CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

Thermodynamic Data Bank: The Principles, Organization, and Structure of Software

K. G. Morgunov

Sobolev Institute of Geology and Mineralogy, Siberian Division, Russian Academy of Sciences, Novosibirsk, Russia

e-mail: morgynov@uiggm.nsc.ru

Received October 29, 2008; in final form, July 20, 2009

Abstract—The structure and special features of a software for work with a data bank are described. A method for storing thermodynamic information about mineral and gas phases and solution components is suggested. The purpose of the creation of the data bank was the provision with the initial thermodynamic data and programs that minimized the Gibbs energy for the solution of physicochemical simulation problems and the construction of mineral equilibrium diagrams. The possibilities of the software were demonstrated for the example of the construction of mineral equilibrium diagrams for minerals containing rare-earth metals.

DOI: 10.1134/S0036024410050031

INTRODUCTION

One of important problems of provision with thermodynamic information for solving physicochemical simulation problems is the dissemination of available and reliable handbook data on the basis of computer data banks. Currently, several popular programs for work with thermodynamic data bases are used in our country and abroad. Among the best known programs, we can mention the Selektor package [1] and the UNITHERM data base built into the HCH program-information package developed at Moscow State University [2]. The SUPCRT98 [3] data base and the IVTANTERMO multipurpose program [4] for solving high-temperature thermodynamic simulation problems are also well known. We must also mention studies [5] for creating a data bank for computer simulation of the evolution of physicochemical processes in high-temperature systems taking into account selective magmatic differentiation mechanisms.

Although these program-information packages for physicochemical simulation of natural processes and work with thermodynamic data banks have found extensive use, the direction related to the creation of software for solving particular special problems has been developing during recent years. Indeed, the existing software does not cover the whole spectrum of problems that must be solved by computer simulations of thermodynamic processes. Such applied problems are calculations of chemical equilibria with the inclusion of adsorption processes, physicochemical simulation of systems containing concentrated solutions of salts, the construction of mineral equilibrium diagrams, the creation of water–rock interaction models taking into account the kinetics of solution of solid phases, etc.

The purpose of this work was to describe the concept, special features of the architecture, and possibilities of the created thermodynamic data bank. We demonstrate the possibilities of using the created software for solving applied geochemical problems, such as the construction of mineral equilibrium diagrams and the obtainment of corrected thermodynamic data on systems containing low-polarity gases on the basis of the equation of state for a fluid.

THE ORGANIZATION, CONCEPT, AND ARCHITECTURAL FEATURES OF THE THERMODYNAMIC DATA BANK

The appearance of mathematically grounded equations of state that allow us to calculate the thermodynamic characteristics of physicochemical system components substantially broadened the temperature and pressure ranges for predicting these characteristics to 1000°C and 5 kbar inclusive. These are primarily the Helgeson–Kirkham–Flowers (HKF) equation for solution components [6, 7] and the Helgeson equation for gases and solids [8, 9].

The software for work with thermodynamic data banks presented in this paper was developed on the basis of the principles built into program packages widely used for solving thermodynamic simulation problems such as Selektor, HCH, and SUPCRT 92-98. The object-oriented Pascal language incorporated into the Delphi package for fast development of applications allows this problem to be solved most effectively. The selected format for the representation of Microsoft Access data is convenient because of its wide-spread use and availability in the Windows user environment. The architectural features of the information stored in the data bank are schematically shown in Fig. 1.

The data bank includes the thermodynamic data on 1287 solution components and 162 solid and 18 gas phases. The data bank is based on the data taken from the SUPCRT98 data bank and augmented by the data on rare-earth metal-containing minerals from [10].

The interaction of the algorithm designed for solving physicochemical simulation problems with the thermodynamic data bank can be described by the following sequence of operations:

—the introduction of system parameters and selection from BASE 1 and BASE 2 of the required aqueous solution components, solids, gas phases, and data necessary for the formation of the initial information file;

—the creation of the initial data file for calculations of the HKF parameters corresponding to the data found in the BASE 1 and BASE 2 data bases and the parameters of the equation of state of the solid and gaseous phases from the SPECIES and COMPONENT data fields;

—the use of the COMPOSITE procedure for finding the elemental composition vector for the description of the stoichiometry of all the chemical and mineral forms present in the system;

—the use of the COMPOSITE procedure for transforming the initial concentrations introduced into the gross elemental composition;

—the determination of solution component charges with the use of the CHARGE procedure;

—the use of the STEHIOMETRY procedure for the formation of the stoichiometric matrix from the elemental composition vector and the list of system components introduced;

—the creation of the stoichiometric information file;

—calculations of the thermodynamic characteristics of system components using the THERM procedure;

—the formation of the data file containing the thermodynamic potentials of system components and other necessary data;

—start of the program for thermodynamic calculations and data output.

A scheme of the interaction of the software with thermodynamic data bases is shown in Fig. 2.

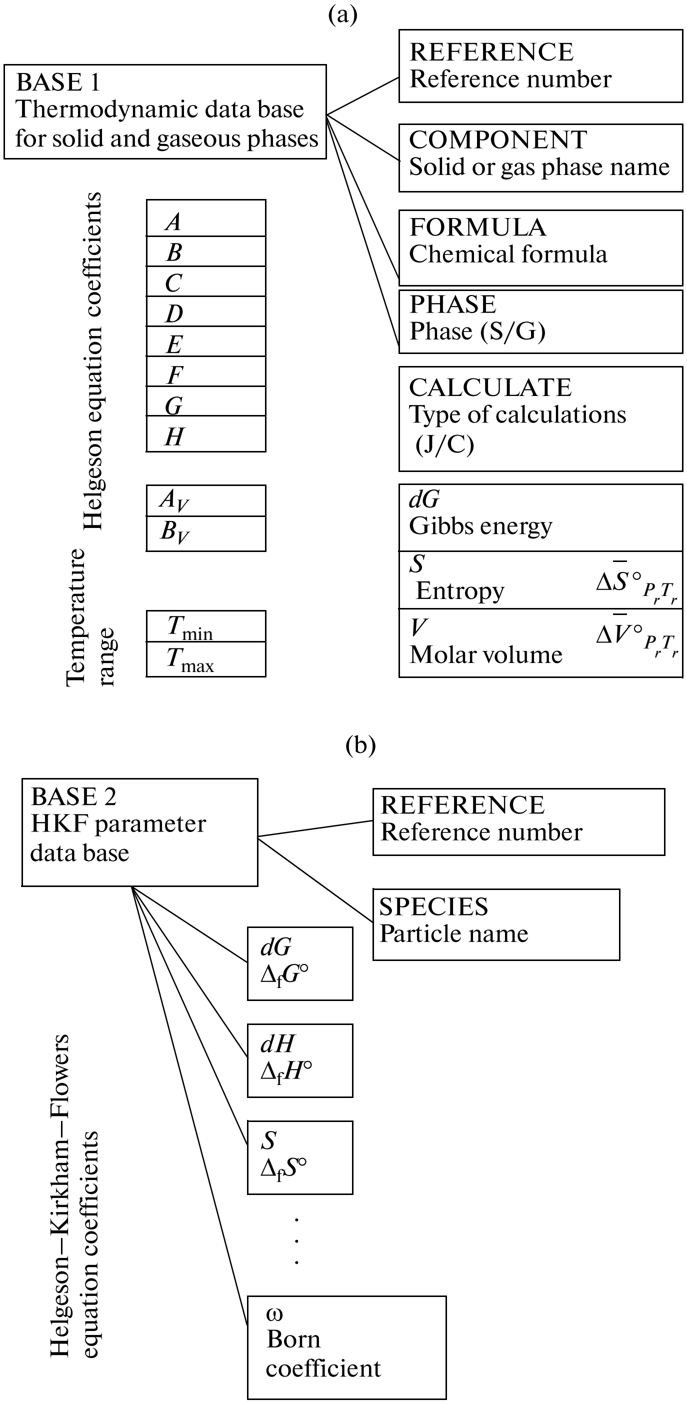

Fig. 1. BASE 1 and BASE 2 data base files (the first row is the name of the field in the data base).

THERMODYNAMIC CHARACTERISTIC CALCULATIONS

The concept of the correlation algorithm suggested by Helgeson, Kirkham, and Flowers [6, 7] contains the general assumption according to which any standard thermodynamic property of a dissolved component (enthalpy, entropy, molar volume, heat capacity, and Gibbs energy) $\Delta\Xi_k^\circ$ is the sum of the solvation $\Delta\Xi_{s,k}^\circ$ and nonsolvation $\Delta\Xi_{n,k}^\circ$ components,

$$\Delta\Xi_k^\circ = \Delta\Xi_{s,k}^\circ + \Delta\Xi_{n,k}^\circ. \quad (1)$$

It is assumed that the solvation contribution to the thermodynamic properties of solution components is

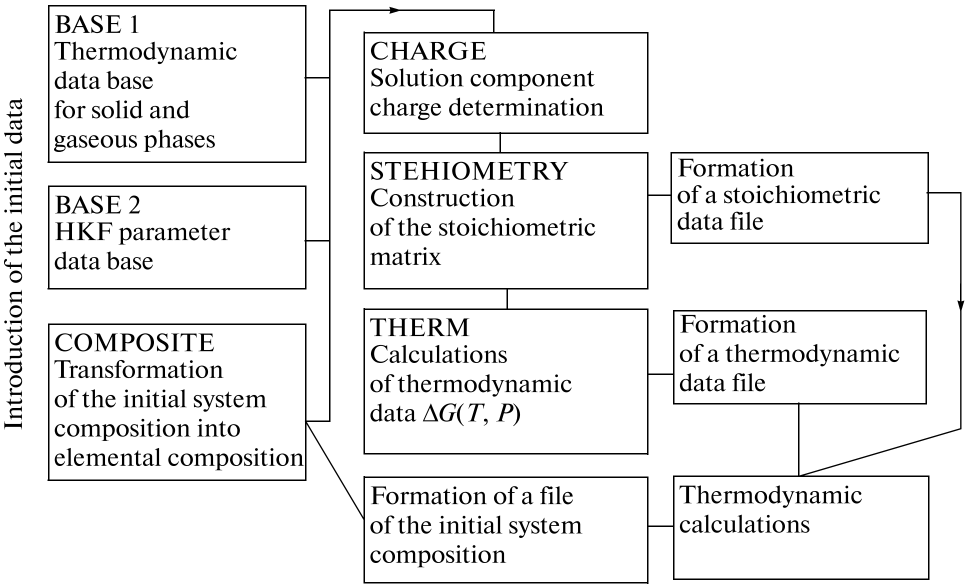

Fig. 2. Scheme of interaction of the software with thermodynamic data bases.

determined by the Born equation for the Gibbs energy,

$$G_{\text{solv}} = \omega(1/\varepsilon - 1), \tag{2}$$

where G_{solv} is the solvation contribution to the Gibbs energy, ω is the Born coefficient, and ε is the permittivity of the solvent. The nonsolvation contribution to the standard thermodynamic property of a solute is in turn calculated as a function of temperature and pressure using the polynomial that approximates the experimental data on the thermodynamic properties of solution components. The equation for calculating the Gibbs energy at the selected T and P thermodynamic parameters has the form

$$\begin{aligned}\Delta\bar{G}^\circ_{PT} &= \Delta G^\circ_{P_rT_r} - \Delta S_{P_rT_r}(T - T_r)\\ &- c_1\left[T\ln\left(\frac{T}{T_r}\right) - T + T_r\right] + a_1(P - P_r)\\ &+ a_2\ln\left(\frac{\psi + P}{\psi + P_r}\right) - c_2\left\{\left[\left(\frac{1}{T - \Theta}\right) - \left(\frac{1}{T - \Theta}\right)\right]\right.\\ &\left.\times\left[\frac{\Theta - T}{\Theta}\right] - \frac{T}{\Theta^2}\ln\left[\frac{T_r(T - \Theta)}{T(T_r - \Theta)}\right]\right\}\\ &+ \left[\frac{1}{T - \Theta}\right]\left[a_3(P - P_r) + a_4\ln\left(\frac{\psi + P}{\psi + P_r}\right)\right]\\ &+ \omega_{PT}\left[\frac{1}{\varepsilon_{PT}} - 1\right] - \omega_{P_rT_r}\left[\frac{1}{\varepsilon_{P_rT_r}} - 1\right]\\ &+ \omega_{P_rT_r}Y_{P_rT_r}(T - T_r),\end{aligned} \tag{3}$$

where $\Delta\bar{G}^\circ_{P_rT_r}$ and $\Delta\bar{S}^\circ_{P_rT_r}$ are the standard Gibbs energy of particle formation and the standard molar entropy of the particle at the P_r and T_r reference values; a_i stands for the temperature- and pressure-independent coefficients that characterize a water particle in the equation of state; c_1 and c_2 are the coefficients individual for each solution particle; ψ and Θ are the solvent parameters assumed to be 2600 bar and 228 K, respectively; ε_{PT} and $\varepsilon_{P_rT_r}$ are the solvent permittivities at current P and T and reference P_r and T_r values, respectively; $Y_{P_rT_r}$ is the partial derivative of solvent permittivity at the P_r and T_r reference values; and ω_{PT} and $\omega_{P_rT_r}$ are the conventional Born coefficients at the current P and T and reference P_r and T_r values.

Calculations of the thermodynamic properties of solids and gas phases were based on the use of the function called the "apparent" standard molar Gibbs free energy [8]. The equation for this function at the required T and P thermodynamic parameters had the form [9]

$$\begin{aligned}\Delta\bar{G}^\circ_{P_rT_r} &= \Delta_f\bar{G}^\circ - \Delta\bar{S}^\circ_{P_rT_r}(T - T_r) - (aA_G + bB_G\\ &+ cC_G + dD_G + eE_G + fF_G + gG_G + hH_G) + \Delta\bar{V}^\circ_{P_rT_r}\\ &\times[1 + A_V(T - T_r) + B_V(T - T_r)^2 + C_V(T - T_r)^3]\\ &\times\left(P - \frac{1}{2}a_VP^2 + \frac{1}{3}b_VP^3\right),\end{aligned} \tag{4}$$

where $\Delta_f\bar{G}^\circ$, $\Delta\bar{S}^\circ_{P_rT_r}$, and $\Delta\bar{V}^\circ_{P_rT_r}$ are the standard Gibbs energy of formation of substances, entropy, and molar volume at the reference pressure and temperature values P_r and T_r; A_V, B_V, and C_V are the empirical coefficients obtained by regression treatment of the temperature dependence of molar volume; and a, b, c, d, e, f, g, h, a_V, and b_V are empirical coefficients individual for each substance. The equations for calculating the A_G–H_G coefficients have the form

$$A_G = T\ln T - T - T\ln T_r + T_r, \tag{5}$$

$$B_G = (T - T_r)^2/2, \tag{6}$$

$$C_G = (T - T_r)^2/2(TT_r^2), \tag{7}$$

$$E_G = ((1/6)T^2 - (1/2)T_r^2 + T/3T_r^3) \times 10^{-6}, \tag{8}$$

$$F_G = (T^3/12 + T_r^4/4 - TT_r^3/3) \times 10^{-9}, \tag{9}$$

$$G_G = 2 \times 10^2\left[\frac{(\sqrt{T} - \sqrt{T_r})(\sqrt{T} - \sqrt{T_r})}{\sqrt{T} - \sqrt{T_r}}\right], \tag{10}$$

$$H_G = (T^5/20 + T_r^5/5 - TT_r^4/4) \times 10^{-12}. \tag{11}$$

A detailed description of calculations of the thermodynamic properties of solution components and solid and gaseous phases can be found in [6–9].

THE EQUATION OF STATE OF A FLUID CONTAINING LOW-POLARITY GASES

The influence of carbon dioxide and other low-polarity gases on internal equilibria in a fluid raises the problem of calculating the influence of corrections for low-polarity gases on the thermodynamic characteristics of solutes. Mathematical models describing the thermodynamic characteristics of mixed fluids use various equations of state for gas mixtures. Among such equations, the best known ones are the Redlich–Kwong equation, whose form resembles that of the ideal gas equation of state; the Holloway–Flowers equation, which is the most theoretically grounded version of the Redlich–Kwong equation; the Kerrick–Jacobs equation of state adapted for H_2O–CO_2–CH_4 mixtures; and the Saxen–Fey model having the form of a virial equation of state with the explicitly written pressure dependence of volume [9]. We used the Redlich–Kwong equation in our calculations.

Let us consider a general scheme of calculating corrections to the thermodynamic properties of solution components for the example of an H_2O–CO_2 mixture most typical of hydrothermal systems. The correction to the properties of the H_2O–CO_2 solvent over the temperature range 100–400°C for changes in the Gibbs energy of solvation of solutes is quite satisfactorily described by the equation [11]

$$G_{\text{solv}} = \omega(1/\varepsilon_{H_2O-CO_2} - 1/\varepsilon), \tag{12}$$

where $\varepsilon_{H_2O-CO_2}$ is the permittivity of the mixed solvent.

The permittivity of mixtures of polar (H_2O) and nonpolar (CO_2) molecules is calculated according to the Loyenga equation [12]

$$\varepsilon = ((\varepsilon_{CO_2}^{1/3} - \varepsilon_{H_2O}^{1/3})V_{CO_2}^f + \varepsilon_{H_2O}^{1/3})^3, \tag{13}$$

where $V_{CO_2}^f$ is the volume fraction of CO_2 in the mixture.

The V_{H_2O} and V_{CO_2} molar volumes of the pure components are calculated using the Redlich–Kwong model [13] by the equation

$$\begin{gathered} PV^3 - RTV^2 - (bRT + b^2P - a/T^{0.5})V \\ - ab/T^{0.5} = 0, \end{gathered} \tag{14}$$

where T is the temperature, P is the pressure, R is the universal gas constant, a is the coefficient represented in the form of an approximating equation as a function of temperature [14], and the b coefficient is set at 1.465 for H_2O and 3.057 for CO_2. The correction to the nonideal electrostatic component of the Gibbs energy is in turn calculated by the equations for the A and B coefficients of the Debye–Hückel equation for activity coefficients from the permittivity of the mixed solvent $\varepsilon_{H_2O-CO_2}$ found by Eq. (4). A detailed description of the numerical scheme for determining corrections introduced by low-polarity gases into the thermodynamic properties of solution components was given in [15, 16].

THERMODYNAMIC POTENTIAL MINIMIZATION AND THE DETERMINATION OF THE EQUILIBRIUM AND PHASE COMPOSITION

The algorithm for thermodynamic potential minimization selected for solving thermodynamic simulation problems is based on the Lagrange method of indefinite coefficients suggested by White [17] and developed by Shimazu [18], Karpov [19], et al.

Thermodynamic equilibrium of a system corresponds to such quantities x_j of solution components and substance in phase α that, at a constant pressure and temperature, correspond to the minimum Gibbs energy value

$$G(x) = \sum_{j=1}^{n}\frac{g_jx_j}{RT} + \sum_{j=1}^{n}x_j\ln\frac{x_j}{X_\alpha} + \sum_{j=1}^{n}x_j\ln\gamma_j, \tag{15}$$

where g_j is the standard isobaric-isothermal potential of one mole of component j at the given temperature and pressure, γ_j is the activity coefficient of component j (which is defined as the initial data or calculated by Debye–Hückel equation in second approximation [9]), and X_α is the total amount of substance in phase α,

$$X_\alpha = \sum_{j=1}^{n} x_j. \tag{16}$$

Limitations to Eq. (15) are the law of conservation of substance and nonnegative molar amounts x_j of solution components and substance in phase α,

$$\begin{gathered} x_j > 0, \\ b_i = \sum_{j=1}^{n} a_{ij} x_j, \end{gathered} \tag{17}$$

where b_i is the total (overall) molar amount of the ith component and a_{ij} is the stoichiometric coefficient corresponding to the number of atoms of the ith chemical element in a molecule of the jth system component.

Calculations by the Lagrange method of indefinite coefficients start with some initial approximation y_j to x_j. A system of linear algebraic equations with respect to Lagrange coefficients u_i and U_α is then solved,

$$\begin{gathered} -\sum_{j=1}^{n} a_{ij} f_j + N_i^\alpha U_\alpha + \sum_{j=1}^{n} u_i r_{ij} - c_j = 0, \\ \sum_{i=1}^{m} N_i^\alpha u_i = \sum_{j=1}^{n} f_j, \end{gathered} \tag{18}$$

where

$$r_{ik} = r_{ki} = \sum_{j=1}^{n} a_{ij} a_{kj} y_j,$$

$$N_i^\alpha = \sum_{j=1}^{n} a_{ij} y_j, \tag{19}$$

$$f_i = \nu_i y_i,$$

$$\nu_j = (g_j/RT + \ln\gamma_j) + \ln(y_i/Y_\alpha).$$

Here, Y_α is the total amount of substance in phase α at the next $(r+1)$th step of calculations. The u_i and U_α solutions to Eqs. (18) are used to find new approximations,

$$x_j = -f_j y_j + (U_\alpha + 1) y_j + y_j \sum_{j=1}^{m} u_i a_{ij}. \tag{20}$$

The scheme for finding the equilibrium composition includes the following steps:

(1) setting initial approximations;

(2) solving system of linear equations (18) with respect to the u_i and U_α Lagrange coefficients;

(3) finding new approximations x_j^{r+1} according to (20) and checking the condition of their nonnegativeness;

(4) correction of y_j^{r+1} to exclude negative values in the iteration process based on the algorithm suggested in [18];

(5) checking the convergence condition $\left|y_j^r - y_j^{r+1}\right| \le \varepsilon$. If this condition is not satisfied, the procedure returns to step (2).

An analysis of the phase composition of the system is performed using the condition of solution saturation with respect to the given solid phase. A scheme of the search for equilibrium association of phases includes the following steps:

(1) calculations of equilibrium in the system with the given phase composition;

(2) determination of solution saturation with respect to the jth mineral phase using the condition $\prod_{j'} (x'_{j'})^{\nu_{j'}} \ge 10^{Lk_j}$, checking the condition of the nonnegative and nonzero molar amount of component $x_j^s > 0$, $x_j^s \ge 10^{-19}$. Here, $\nu_{j'}$ is the stoichiometric coefficient of the reaction between the mineral and solution and Lk_j is the rate constant for the solution of the jth mineral phase;

(3) return to step (1) if the phase is excluded from the system;

(4) completion of the iteration procedure and output.

THE CONSTRUCTION OF A DIAGRAM OF MINERAL EQUILIBRIA

The algorithm for finding boundaries in the coordinates of concentrations corresponding to a change in the phase composition of a system was constructed by combining the algorithm for segment bisection modified for solving this problem and the algorithm for thermodynamic potential minimization. Calculations according to the suggested scheme start with preliminary calculations aimed at determining the approximate location of the regions of mineral phase stability in the diagram to be constructed. For this purpose, the sought diagram is covered with a grid with a selected

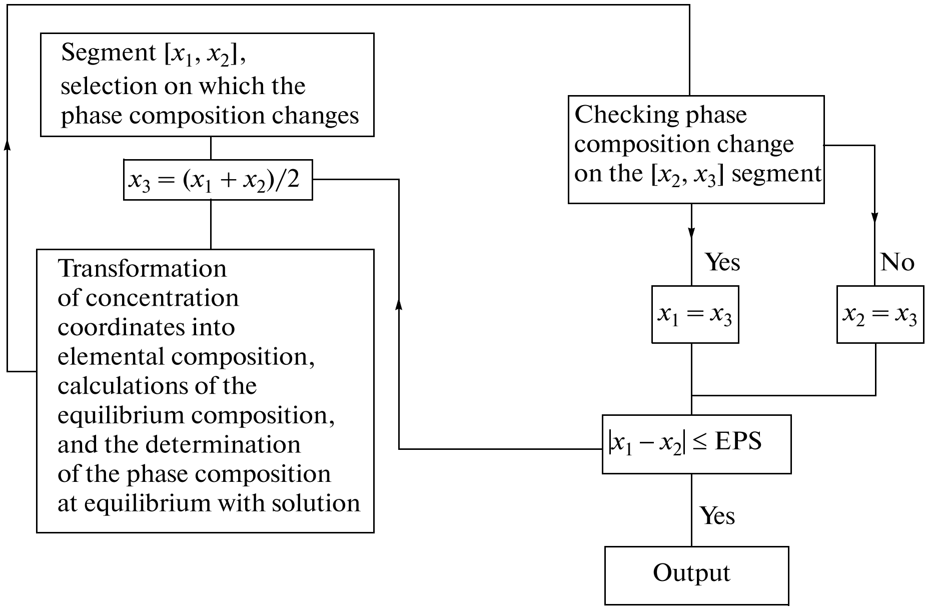

Fig. 3. Scheme of the procedure for determining the point corresponding to a change in the phase composition of the system in concentration coordinates.

concentration step, and equilibria at nodal points are calculated. After the approximate location of mineral phase stability regions is found, calculations by the segment bisection algorithm are performed. The points in the coordinates of concentrations are approximated by a power polynomial. The data obtained at intermediate points and the polynomial found are used to construct lines corresponding to diagram phase boundaries. The scheme of calculations for finding the concentration coordinates of a point corresponding to a change in the phase composition of the system is shown in Fig. 3.

NUMERICAL EXAMPLES OF THE USE OF THE SUGGESTED SOFTWARE IN PRACTICE

The created software was primarily used to simulate the behavior of rare-earth metals and construct equilibrium diagrams for minerals that precipitate rare-earth metals. A visual example characterizing the suggested software is the stability diagrams for fluorite–calcite–F-apatite and OH-apatite minerals and numerical simulation of the behavior of rare-earth metals and yttrium in a variable-composition high-temperature hydrothermal fluid. The diagram of the fields of stability of minerals precipitating rare-earth metals was constructed for a solution equilibrium with Ca-containing minerals. The concentrations were $CaCl_2$(s) 10^{-3}, carbonic acid H_2CO_3 from 10^{-4} to 0.4, HCl from 10^{-4} to 0.1, NaOH from 10^{-4} to 0.5, HF 0.01, and phosphoric acid H_3PO_4 0.001 (here and throughout, all the concentrations are given in mol/kg H_2O).

The equilibrium diagram of calcite–fluorite–OH-apatite minerals at 100°C and 1 kbar is shown in Fig. 4. The model system used to describe the behavior of rare-earth metals and yttrium in a high-temperature hydrothermal fluid was a solution with the concentrations HCl, 0.01; H_2CO_3 0.01; and NaOH from 0.1 to 0.001. The mineral composition included fluorite in a concentration of 1.0, rare-earth metals, and Ce and Y fluorites in concentrations of 1.0×10^{-3}. The dependence of the solubility of several rare-earth metal-containing phases, Y fluorite, fluorite, and calcite on the mole fraction of CO_2 changing in the system is shown in Fig. 5.

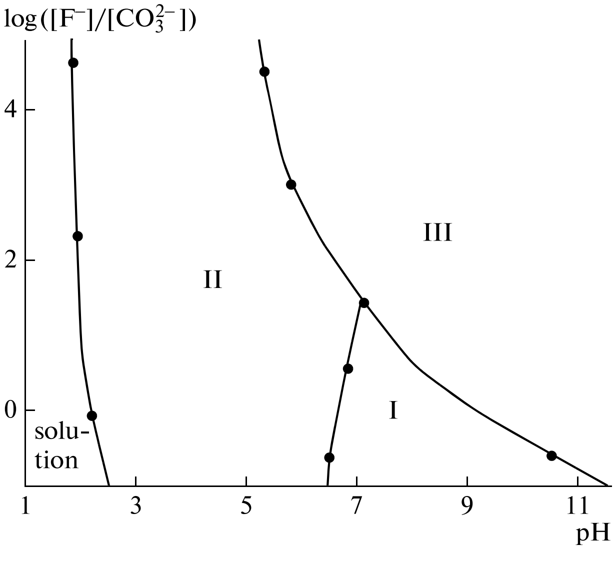

Fig. 4. Equilibrium diagram for calcite (I), fluorite (II), and OH-apatite (III) minerals at 100°C and 1 kbar.

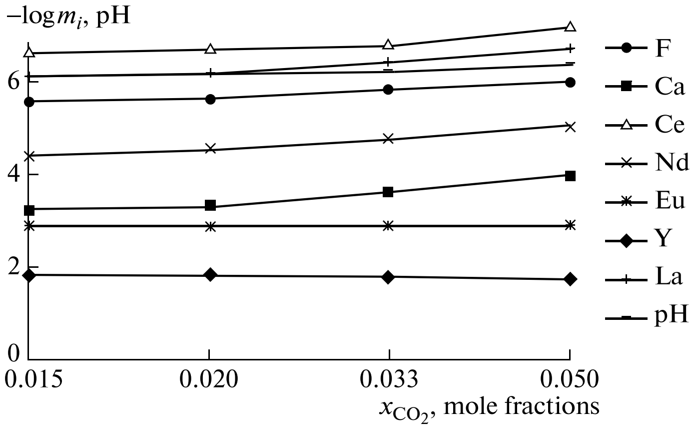

Fig. 5. Solubility of rare-earth metal-containing phases at 400°C and 1 kbar.

CONCLUSIONS

The suggested paper continues works concerned with the creation of a thermodynamic data bank [20, 21]. The mathematical models and software designed for work with relational thermodynamic data bases and the package of programs for constructing mineral equilibrium diagrams and obtaining corrected thermodynamic data on systems containing low-polarity gases can be used to substantially broaden the range of problems that can be solved using the algorithm for thermodynamic potential minimization.

The program-informational complex created on the basis of thermodynamic data bases in our view provides additional possibilities, which facilitate and simplify numerical physicochemical simulation experiments for a wide range of possible users.

ACKNOWLEDGMENTS

The author thanks V.N. Sharapov and V.P. Il'in for cooperation and help with developing the concept of a thermodynamic data bank. This work was financially supported by the Ministry of Science and Eduacation of Russian Federation, grant RNP 2.1.1.702, and the Russian Foundation for Basic Research (project no. 07-05-00685).

REFERENCES

1. K. V. Chudnenko, Extended Abstract of Doctoral Dissertation in Technical Science (Ivanovo, 2007).
2. M. V. Borisov, *Geochemical and Thermodynamical Models of Vein Hydrothermal Ore Formation* (Nauchn. Mir, Moscow, 2000) [in Russian].
3. J. Johnson, E. Oelkers, and H. Helgeson, Comput. Geosci. **18**, 899 (1992).
4. G. V. Belov, *Thermodynamic Modeling* (Nauchn. Mir, Moscow, 2002) [in Russian].
5. M. S. Ghiorso and I. S. E. Carmichael, Contrib. Mineral. Petrol. **90**, 121 (1985).
6. E. L. Shock and H. C. Helgeson, Geochim. Cosmochim. Acta **52**, 2009 (1988).
7. J. C. Tanger IV and H. C. Helgeson, Am. J. Sci. **288**, 19 (1988).
8. P. I. Dorogokupets and I. K. Karpov, *Thermodynamics of Minerals and Mineral Equilibria* (Nauka, Novosibirsk, 1984) [in Russian].
9. *Thermodynamic Modeling of Geologic Materials: Minerals, Fluids and Melts*, Ed. by I. S. E. Carmichael and H. P. Eugster (Mineralog. Soc. Amer., Washington, 1987; Mir, Moscow, 1992).
10. *Handbook on the Physics and Chemistry of Rare Earths*, Ed. by O. Greis and J. M. Haschke (North-Holland, Oxford, Amsterdam, New York, 1982), pp. 460.
11. N. N. Akinfiev, Geokhimiya, No. 10, 1465 (1994).
12. H. Loyenga, Phys. **31**, 401 (1965).
13. O. Redlich and J. N. S. Kwong, Chem. Rev. **44**, 233 (1949).
14. T. J. B. Holland and R. Powell, J. Metamorphic Geol. **3**, 343 (1985).
15. G. R. Kolonin, G. A. Pal'yanova, G. P. Shironosova, and K. G. Morgunov, Geokhimiya, No. 12, 1725 (1994).
16. G. R. Kolonin, G. A. Pal'yanova, G. P. Shironosova, and K. G. Morgunov, Geokhimiya, No. 1, 46 (1997) [Geochem. Int. **35**, 40 (1997)].
17. W. B. White, S. M. Johson, and G. B. Dantzig, J. Chem. Phys. **25**, 751 (1958).
18. Y. Shimazu, "Thermodynamical Aspects of Formation Processes of the Terstrial Planets and Meteorites," Icarus **6**, 143 (1967).
19. I. K. Karpov, *Physicochemical Numerical Modeling in Geochemistry* (Nauka, Novosibirsk, 1981) [in Russian].
20. K. G. Morgunov, Extended Abstract of Candidate's Dissertation in Geology and Mineralogy (Novosibirsk, 2006).
21. G. R. Kolonin, K. G. Morgunov, and G. P. Shironosova, Geol. Geofiz. **42**, 881 (2001).