PhDi—Software package for calculation of binary phase diagrams

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Abstract

A new algorithm for the calculation of phase diagrams based on the method of convex hulls is presented. The computer program and database for thermodynamic modeling of binary systems are described and examples of calculated phase diagrams are given.
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1. Introduction

Phase diagrams are extensively used nowadays in science and industry. The existing methods and software packages for the calculation of phase diagrams are reviewed in several publications, e.g. [1,2]. Using the traditional approach one should solve many times the phase equilibrium problem in order to draw the phase diagram. The procedure of calculations of such kind is similar to the competition among all possible phases, and at given physical conditions only some of the many phases can exist in an equilibrium system. The physical conditions are determined by thermodynamic variables: pressure, temperature, and number of moles of components, and the values of characteristic thermodynamic functions serve as the criteria for phase existence. It should be noted that phases do not compete among themselves. The competition occurs between states of the system which consist of various sets of phases. The most stable set of phases is the one which provides the minimal value of the characteristic function of system. A minimization of the Gibbs energy procedure is used in most cases to determine the phase composition at given pressure, temperature and number of moles of the components.

2. Methods

2.1. The principle of calculation of phase diagrams

In our package, instead of conditional minimization of the thermodynamic potential of the system, the convex hull approach is used. The theoretical basis and the possibilities of the new method are described in Refs. [3,4]. This method is based on using the convexity properties of the envelope of the thermodynamic potentials for constructing phase diagrams directly from the initial thermodynamic data and the computational geometry for calculating convex hulls. Thus there is no need to solve nonlinear equations or systems of nonlinear equations or to minimize characteristic functions which is necessary in other methods of calculation of phase equilibria. There is no need to assign an initial guess for computed parameters. Such an approach is very effective for an analysis of systems that consist of individual phases. Solutions of the components are treated in the program as a set of individual compounds of various concentrations, and each compound has such a value of the characteristic function that it coincides with the value of the function for a solution of the corresponding composition. Actually, the phase diagram is computed at a user-specified grid of nodes, and the accuracy of the calculations depends on the density of the grid. The higher is the density of the grid, the better is the accuracy of the calculations, but the longer is also the time required for the calculation.

2.2. Algorithm of calculation

The general idea of the algorithm consists of the calculation of the convex characteristic function of the system using values of characteristic functions of phases that are in a position to exist in the system. Consider now the algorithm of the calculation of the phase diagram of a binary system in coordinates Y–x, where Y is an intensive thermodynamic parameter that specifies a characteristic function of the phase (temperature, pressure, etc.), and x is the mole

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fraction of one of the components or any other extensive (quasi-extensive) variable:

(1) Assign the range of variation for Y and x coordinates. The mole fraction range of variation is usually given by the interval 0–1.
(2) Assign the number of node points for Y and x coordinates, which specify the step values ΔY and Δx and hence the accuracy of the calculations.
(3) Organize two (outer and inner) iterative cycles. In the outer cycle the parameter Y is varied from Y_{min} to Y_{max} with the step ΔY, and in the inner cycle the calculation of the characteristic function value of all phases of the system is accomplished. In the calculations in the inner cycle the current value of Y is used and the x parameter is varied from x_{min} to x_{max} with the step Δx.
(4) On the Y coordinate after each iteration we obtain a set of values of characteristic functions that describe the primary thermodynamic surfaces of phases that form the system. Then we find those points from the set which belong to the convex hull of it using some convex hull algorithm. The lower part of this convex hull describes the surface of the used thermodynamic potential at equilibrium.
(5) Analyze the set of points that form the convex hull and determine the phase composition in each of them taking into account that if the convex hull in some point coincides with the primary thermodynamic surface of some phase then in this point there is only this phase. If the distance between two neighbor points exceeds Δx then in the interval between them is heterogeneous equilibrium. In the general case, the heterogeneous field is formed by those phases that exist at the left and right margins of this field. As a result of the analysis we obtain coordinates of points in which the change of phase composition takes place.
(6) After accomplishing one step at the Y coordinate we have a fragment of the phase diagram having the height ΔY at the interval $[x_{min}, x_{max}]$. The phase diagram itself consists of the set of points in which the phase composition changes. So when the outer cycle is finished we have the whole phase diagram in coordinates Y–x.

2.3. Software package PhDi

The algorithm presented was used for the development of the software package PhDi, which comprises the computer program and database on thermodynamic properties of binary systems. The program allows computing phase diagrams of:

(1) unary systems in coordinates temperature-molar volume (density) at fixed pressure and pressure-molar volume (density) at fixed temperature;
(2) binary systems in coordinates temperature-composition at fixed pressure and pressure-composition at fixed temperature;
(3) multi-component quasi-unary and quasi-binary systems corresponding to cases (1) and (2), e.g. ternary open systems with a given partial pressure of one of the components.

In order to compute the phase diagram one should (1) establish the coordinates of the phase diagram and the extent of their variations, (2) type or find in the data base the analytical expressions of the appropriate characteristic functions (Gibbs energy, Helmholtz energy) of all possible phases of the system as functions of their natural variables (temperature, pressure, volume, composition, etc.), and (3) specify a grid of points for the development of the diagram (e.g. 100×100). The computed diagrams correspond to thermodynamically stable states of the system. Besides the graphical representation of the diagram, the program computes also coordinates of special points, where the phase composition changes and breaks the smoothness of the curves describing equilibrium. There are several auxiliary functions of the program for the visualization of the process of calculation and presentation of its results described in the Users Guide of the software.

2.4. Database on thermodynamic properties of binary systems

The data model created for database development comprises the following entities:
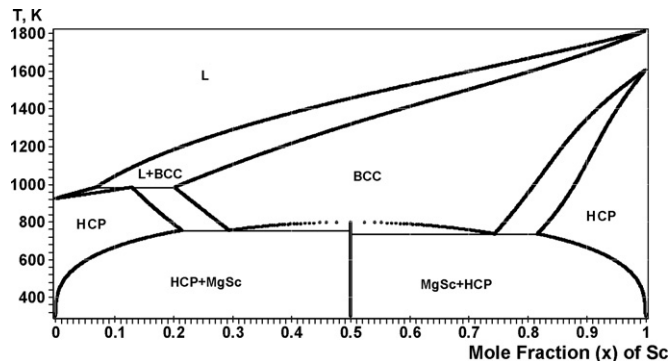

Fig. 1. Calculated phase diagram of the system Mg–Sc.

- SYSTEM: designation, components, kind of Y parameter (temperature or pressure), lower and upper values of Y, number of points on X and Y axes;
- PHASE: phase designation;
- GIBBS ENERGY EXPRESSION (for a given temperature interval): analytical expression of the characteristic function together with the lower and upper temperature values that define the interval where the expression is valid;
- STABILITY PARAMETER (name): designation of stability parameter;
- STABILITY PARAMETER EXPRESSION[1] (for a given temperature interval): analytic expression for the calculation of the Gibbs energy difference between the two phases of the same component, together with the lower and upper temperature values that define the interval where the expression is valid;
- EXPERIMENTAL DATA: data source, experimental values of X and Y coordinates for the phase diagram taken from various sources.

The number of databases is arbitrary, but each of them must be located in a separate directory. Information on Gibbs energies of the phases is stored in database in analytical form. For the presentation of the Gibbs energies of the phases a special language has been developed, which is similar to well known programming language BASIC. The program has a parser that uses typed analytical expressions for calculation of the Gibbs energies of the phases as function of thermodynamic parameters and composition of the system. The main advantage of such an approach is the independence of definite physical models. Besides, the software has built-in utilities for data export and data import operations that provide a possibility of the data exchange among databases. The prepared database contains information on thermodynamic properties of approximately 200 binary and quasi-binary systems (metal–metal mostly). The information in the database was compiled from literature sources. The opportunity of introduction of new data taken from original works or received by the user is possible too.

3. Results

3.1. Examples of the phase diagram calculation

Fig. 1 shows the calculated (T, x) phase diagram of the system Mg–Sc; a (1500×1500) grid of nodes was used. The initial thermodynamic data were taken from Ref. [6]. The system has four phases: liquid (L), solid compound (MgSc) and two solid solutions with body centered (BCC) and hexagonal closed packed (HCP) structures. For example the Gibbs energies (G_i, $i =$ L, BCC, HCP, MgSc) of these four phases relative to the heterogeneous mixture of pure Mg and Sc with HCP-structure are included into the work window of the program as the next records

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[1] The value of this entity may be defined for one or several temperature intervals. It depends on the form these expressions are used in original works (see, for example [5]).

Table 1
Special points of the assessed Mg–Sc phase diagram (see Fig. 1)

Reaction	Compositions of the respective phases, mol fraction of Sc			T (K)
Mg (L) = Mg (HCP)	0			924.5
L + BCC = HCP	0.068	0.128	0.202	982.7
BCC = HCP + MgSc	0.214	0.296	0.500	756.2
BCC = MgSc		0.500		797.1
BCC = MgSc + HCP	0.500	0.742	0.818	737.3
Sc (L) = Sc (BCC)			1	1813.2
Sc (BCC) = Sc (HCP)			1	1605.6

(the developed language is used for the Gibbs energy dependence presentation):

$$G_L = (1-x)(\{Mg\_L–HCP\}) + x(\{Sc\_L–HCP\}) − T \text{ Sid}$$
$$+x(1-x)(−12000.0 + 8.75T) \qquad (1)$$

$$G_{MgSc} = −21926.0 + 2.0T + 2.649T \ln(T) \qquad (2)$$

$$G_{BCC} = (1-x)(\{Mg\_BCC–HCP\}) + x(\{Sc\_BCC–HCP\})$$
$$−T \text{ Sid} + x(1-x)(−24051.0 + 15.56T) \qquad (3)$$

$$G_{HCP} = −T \text{ Sid} + x(1-x)(−16115.8 + 15.02T) \qquad (4)$$

where "T" and "x" are the temperature and the mole fraction of the second component, "Sid" is the ideal mixing entropy, i.e. $−R[(1-x)\ln(1-x) + x \ln x]$. The entities in {} are the expressions of the stability parameters of the components. They are available in the database and equal to the Gibbs energies of the phase transitions "HCP → L" and "HCP → BCC" in the pure metals. Eqs. (1)–(4) are the input lines, which are used in the program for calculation of the Gibbs energy of the phases.

The names of the phases are indicated in Fig. 1 by means of pressing the right mouse button on the appropriated fields of the calculated diagram. Calculated coordinates of the special points of the assessed diagram are shown in Table 1.

Fig. 2 shows the calculated phase diagram of the ternary system K–Na–Cl$_2$ at a fixed temperature $T = 630$ K. This sys-
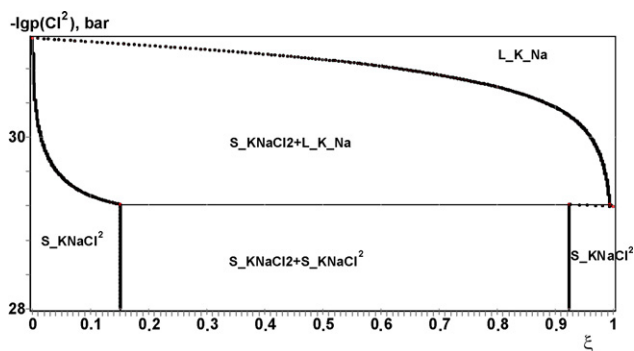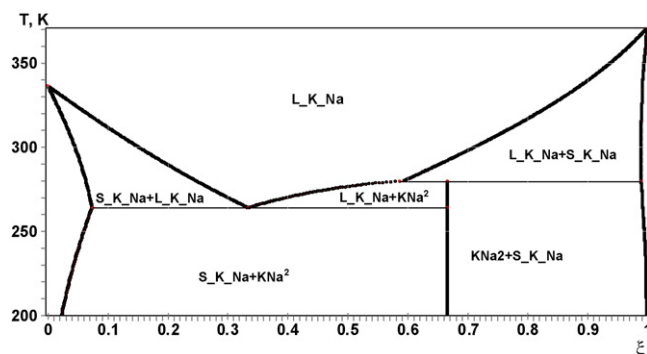

Fig. 3. T–ξ diagram of the ternary K–Na–Cl$_2$ system at $p(Cl_2) = 10^{−120}$ bar.

tem contains the following phases: solid solution KCl–NaCl (S_KNaCl$_2$) with miscibility gap, liquid solutions KCl–NaCl (L_KNaCl$_2$), K–Na (L_K_Na), solid solution K–Na (S_K_Na) and compound KNa$_2$ (KNa$_2$). The two last phases are unstable at the given values of the thermodynamic variables. It is essential to note that the various phase diagrams can be easily obtained from the same set of Gibbs energies by changing the values of the temperature or of the partial pressure of Cl$_2$. For example, presented in Fig. 3 is the T–x section of the ternary system K–Na–Cl$_2$ at $p(Cl_2) = 10^{−120}$ bar results in the binary K–Na diagram.

A demo version of PhDi program is available on the Web page http://td.chem.msu.ru/.

Acknowledgements

Fig. 2. Phase diagram of the ternary K–Na–Cl$_2$ system at $T = 630$ K with coordinates $\lg p(Cl_2)$ and $\xi = n_{Na}/(n_{Na} + n_K)$, n_{Na}, n_K—quantities of corresponding metals.

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