

Program PhDi

User guide

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THE ASSIGNMENT OF SOFTWARE

The software is designed to calculate the phase diagrams of

- one-component systems in coordinates
 - Temperature – Molar volume (or density) at constant pressure;
 - Pressure – Molar volume (or density) at constant temperature;
- binary systems in coordinates
 - Temperature - Composition at constant pressure;
 - Pressure – Composition at constant temperature;
- multicomponent systems which can be reduce to one- or two-component systems corresponding to that in p.1,2.

Thermodynamic properties used to compute the phase diagrams are Gibbs energies (or Helmholtz energies) of all possible phases of the system as functions of temperature, pressure, volume and composition. The computed diagrams correspond to thermodynamically stable states of the system. The results of calculations are presented in graphical form as well as coordinates of special points where the phase composition changes or monotonous character of lines describing equilibrium is violated.

The structure of an information complex includes a database and program PhDi which ensures the functioning with data, gives an opportunity of calculation of phase diagrams and carrying out of the analysis of results of calculations.

The database contains the information on properties of phases approximately 180 binary systems (basically Me – Me). Data from the original works which were not estimated from the point of view of their quality or conformity to real phase diagrams of concrete systems have been used at creation of a database. Intervals of the varied parameter (p, T), significance of the fixed parameter (p, T) and names of phases are installed in conformity with the values which have been accepted in original works.

PRINCIPLE OF CONSTRUCTION OF PHASE DIAGRAMS

To construct the phase diagram, it is necessary to calculate a series of phase equilibria. It is possible to assimilate computing procedure with competition between all basically probable phases, for the right to be presented in equilibrium system under given conditions. Those conditions are defined by thermodynamic variables – temperature, pressure, component composition, and the values of characteristic functions serve as criterion of selection of phases. It is necessary to note, that states of system which arise at different sets of phases, instead of phases compete among

themselves. Advantages have those phases or their combinations which allow optimizing characteristic function of all system corresponding to coordinates of the phase diagram. Usually it is a question of minimization of Gibbs energy of system under the set conditions – pressure, temperatures and component composition.

In this program constrained minimization of thermodynamic potential of system is replaced by construction of convex hulls of thermodynamic potentials of all probable phases¹. Phase equilibrium is computed using the convex envelope of Gibbs energies of phases for various compositions of the system and given pressure and temperature. It is possible to construct such convex hulls for Helmholtz energy as function of molar volumes if the temperature and phase composition are fixed. From a convex hull of set convex function is allocated. According to known theorems, this convex function constructed on set of corresponding thermodynamic potentials, is characteristic function of all system. Camber of such function guarantees performance of conditions of stability for compounds and solutions which thermodynamic potentials have mutual points with convex function.

The computational geometry algorithm is used for construction of convex hulls. Owing to that there is no need to solve the system of equations or find coordinates of constrained Gibbs energy minimum of the thermodynamic system. The solutions of components are presented in the software as a set of individual substances with various compositions and each of them has properties of the solution with corresponding composition. So the phase diagram is computed for user defined grid of points and the accuracy obtained is determined by density of the grid. The more points there are given for each coordinate the more accurate is result, but the more computer resources are necessary.

THE BASIC THERMODYNAMIC DATA

To calculate the diagram, it is necessary to write down the analytical dependences of thermodynamic properties (for example, molar Gibbs energies) as function of their native variables (for example, temperature, pressure, molar fraction of components) for all phases of the system in a working window of the program. As a data source about properties of phases may be used a thermodynamic tables, computer databases, articles, results of experiment, compilation of other data, or purposeful selection of the separate thermodynamic parameters allowing to describe adequately known phase diagram in case of so-called ill-posed thermodynamic tasks. Thus it is necessary to pay special attention on reference state of variables, keeping in mind that ways of representation of the same thermodynamic data can strongly differ, despite of existing recommendations on their standardization. Below in this section the brief and most general information concerning records of thermodynamic data in a working window of the program is presented. The reader having sufficient experience of thermodynamic calculations can omit this section and go immediately to examples at the end of this user guide.

The Reference States

The Gibbs energy and Helmholtz energy of individual substance are functions of temperature and pressure or volume, accordingly. In the case of solution it's necessary to take into account a composition dependence of them too. In process of equilibrium calculation the energies of various phases of system are compared. And such comparison is correct only if all phases have uniform level of energies because the value of any energy is determined within the constant. In the tables of thermodynamic properties the Gibbs energy of individual compound is counted relatively to sum of Gibbs energies of composite chemical elements which make up a heterogeneous mixture with the same composition. Any of those elements are found in the standard conditions at chosen

¹ G.F. Voronin. New Possibilities for Thermodynamic Calculations and Phase Diagram Construction of Heterogeneous Systems // Russian Journal of Physical Chemistry. 2003. V.77. №10, P.1685-1694.

temperature. For example, standard molar Gibbs energy of formation of binary compound A_1-xB_x (A, B – chemical elements) may be written as

$$\Delta_f g^0 = g^0 - [(1-x) \cdot g_A^0 + x \cdot g_B^0], \quad (1)$$

where g^0 , g_A^0 , g_B^0 – molar Gibbs of compound and constituent components in standard state, x – mole fraction of a component B in compound. The expression in square brackets is a standard level of reference (in this case, Gibbs energy) of individual compound which can be applied at the analysis of isobaric-isothermal processes. Different phases, for example, liquid, crystal and gaseous, have differing standard states of components, and, to unify energy levels of all phases of interesting system, it is necessary to know properties of pure components in corresponding liquid, crystal, gaseous states. According to eq.(1) Gibbs energy of individual substance measured relatively uniform level for all set of phases, can be presented in the form of

$$\Delta g^{ref} = \Delta_f g^0 + (1-x)(g_A^0 - g_A^{ref}) + x(g_B^0 - g_B^{ref}). \quad (2)$$

Uniform indexes (0) and (ref), obviously, do not mean that state of A and B are identical; phases of substances A and B may be different. In some cases the states of components in system of comparison can coincide with standard and then corresponding parameters of stability of components ($g_A^0 - g_A^{ref}$, $g_B^0 - g_B^{ref}$) are equaled to zero. An application of eq.(2) can be seen in considered below examples.

Unlike individual substances, standard functions of formation of a solution usually name functions of mixing. They describe process of formation of a solution during mixing of the components which are being the same phase, as a solution. Such choice of reference state provides a continuity of thermodynamic functions of a solution in complete interval of composition, including the boundary pure components (for binary solutions $0 \leq x \leq 1$). That is necessary for performance of laws of ideal-dilute solutions (more precisely – Raoult's law for the solvent). The general expression of Gibbs energy of mixing, $\Delta_{mix} g^k$, for k-th phase of a binary solution

$$\Delta_{mix} g^k = g^k - (1-x)g_A^k - xg_B^k \quad (3)$$

differs from eq.(1) that phases of a solution and components should be identical. However, if to keep in mind that there are a few phases in the interesting system, and the state (k) and uniform reference state of phases may be different, this distinction appears not so essential, as in this case. So, by analogy with eq.(2) it can be written

$$\Delta g^{ref} = \Delta_{mix} g^k + (1-x)(g_A^k - g_A^{ref}) + x(g_B^k - g_B^{ref}). \quad (4)$$

The Lattice Stabilities

Let's admit, for example, that in system A-B exist liquid (l), solid (s) and gas (v) solutions. Gibbs energies of pure liquid components A ($x = 0$) and B ($x = 1$), taken at the same temperatures, pressure and in the same proportions, as in a corresponding solution are accepted as a reference state of $g^l(x)$, $g^s(x)$, $g^v(x)$ functions. For calculating the relative Gibbs energy of every phase and system in general a sum $(1-x)g^l(0) + xg^l(1)$ should be subtracted from the absolute value of corresponding molar Gibbs energy. This sum is corresponding to the first member in right-hand part of equation (3). For a liquid solution such choice, such system of comparison of properties of a solution, coincides with its "natural" standard condition providing a continuity $g^l(x)$, therefore two last members in eq.(4) are equal to zero. Unlike a liquid phase, solid state function - $\Delta g^{s,ref}(x)$ - has thus break of a continuity at the boundary composition. To provide a continuity of Δg^{ref} it is necessary to know a quantity $(1-x)[g^s(0) - g^l(0)] + x[g^s(1) - g^l(1)]$. The functions in square brackets of this expression are parameters of phase transitions of pure components A ($x = 0$) and B($x = 1$),

namely, Gibbs energy changes at their crystallization. As it was already marked, such parameters have received the name "lattice stabilities" of components. In general case lattice stabilities concern to nonequilibrium phase transitions. To not limit calculations by isothermal processes, it is necessary to consider a temperature dependence of these parameters. If it possible to neglect a difference in heat capacities between the phases (for non-wide range of temperatures) an estimation of lattice stability will be such:

$$g^s(0) - g^l(0) = -\Delta_m s_A (T_{m,A} - T) = -\Delta_m h_A \left(1 - \frac{T}{T_{m,A}} \right),$$

$$g^s(1) - g^l(1) = -\Delta_m s_B (T_{m,B} - T) = -\Delta_m h_B \left(1 - \frac{T}{T_{m,B}} \right),$$

where $\Delta_m s$ and $\Delta_m h$ are the molar entropies and enthalpies of melting of components at temperature of fusion T_m . If the necessary data are available it is possible to receive more exact description. Formulas for lattice stabilities of many liquid and crystal phases of chemical elements are given in the articles² and books. The reference state for gaseous solution is a hypothetical state of ideal gas at standard pressure $p^\circ = 1$ bar. If, as well as earlier, Gibbs energies of pure liquid components are accepted as reference state, therefore lattice stabilities become $(1-x)[g^v(0, p^\circ) - g^l(0)] + x[g^v(1, p^\circ) - g^l(1)]$. If components (A and B) may be consider as ideal monatomic gases, then last expression is equivalent to $-RT[(1-x)\ln p_A^s + x\ln p_B^s]$, where p_i^s is the saturated vapor pressure of pure liquid i -th component, $-RT \ln p_i^s = \Delta_v h_i^\circ - T\Delta_v s_i^\circ$, $\Delta_v h_i^\circ$ and $\Delta_v s_i^\circ$ are the standard molar enthalpies and entropies of evaporation. If gaseous phase is not ideal, it is necessary to use fugacity instead of pressure.

A Composition Dependence of Function of Mixing

That functions of mixture "automatically" considered boundary conditions, they can be divided on two parts - "ideal" (id) and "excess" (ex):

$$\Delta_{mix} g = \Delta_{mix} g^{id} + \Delta_{mix} g^{ex}. \quad (5)$$

The Gibbs energy of mixing of ideal liquid or solid solution is common to write as

$$\Delta_{mix} g^{id} = RT[x \ln x + (1-x) \ln(1-x)] = -Ts^{id},$$

and in case of ideal gaseous solution we can write

$$\Delta_{mix} g^{id} = RT[x \ln x + (1-x) \ln(1-x) + \ln p] = -Ts^{id} + RT \ln p,$$

where p is the total pressure above a solution, equal to the sum of partial pressures of components, s^{id} is the ideal entropy of mixing. The introduction of "ideal" member provides observance of laws of ideal-dilute solutions. Sometimes, as in case of the rarefied gases, it allows to exclude "excess" part describing difference between properties of real and ideal solutions. Such differences are absent at boundary compositions. To consider it special member in excess thermodynamic functions is allocated. It may be written as $x \cdot (1-x)$ and equal to zero at boundary composition. The excess Gibbs energy, $\Delta_{mix} g^{ex}$, can be represented by various analytical expressions, for example, as a power series in terms of temperature and composition:

$$\Delta_{mix} g^{ex} = x(1-x) \left[a_0(T) + a_1(T) \cdot (1-2x) + \dots + a_n(T) \cdot (1-2x)^n \right],$$

² Dinsdale A., SGTE data for pure elements // CALPHAD. – 1991. – V.15, № 4. – P.317-425.

where $a_i(T)$ are linear or more complex functions of temperature and, probably, pressure ($i = 0, 1, \dots, n$). There are many other forms of ideal and excess members of Gibbs energy. In particular, models with internal parameters have been applied to solutions with complex composition dependence of thermodynamic functions. With their help it may be possible to express chemical equilibria, an ordering in crystal lattice and other features of an internal structure of a phase. Such parameters have been calculated as a result of optimization of characteristic function of system. In the offered version of the program the models with internal parameters are not stipulated.

DATABASE ON THERMODYNAMIC PROPERTIES OF BINARY SYSTEMS

The data model created for database development consists of the following entities:

- SYSTEM;
- PHASE;
- GIBBS ENERGY EXPRESSION (for given temperature interval);
- STABILITY PARAMETER (name);
- STABILITY PARAMETER ENERGY EXPRESSION (for given temperature interval);
- EXPERIMENTAL DATA.

It is supposed that the system consists of one or several phases, the properties of each phase are defined for one or several temperature intervals and may be restricted by component ratio value. Besides the system may have experimental data describing the phase diagram and taken from various sources. To simplify the analytic expression of characteristic function of system phases such entity as STABILITY PARAMETER is used. The value of this entity may be also defined for several temperature intervals.

Basic features of the database entities are listed below.

1. SYSTEM – designation, components, kind of Y parameter (temperature or pressure), lower and upper values of Y, number of points by X and Y axes;
2. PHASE – phase designation;
3. GIBBS ENERGY EXPRESSION – analytic expression for calculation of the characteristic function of the phase, lower and upper values defining the temperature interval;
4. STABILITY PARAMETER – designation of stability parameter;
5. STABILITY PARAMETER ENERGY EXPRESSION analytic expression for calculation of the characteristic function of the stability parameter, lower and upper values defining the temperature interval;
6. EXPERIMENTAL DATA – data source, experimental values of X and Y coordinates at the phase diagram.
7. Actually the information from database is stored in the following files: *experim_data.d*, *gibbs_energy.d*, *phases.d*, *stability_detail.d*, *stability_params.d*, *systems.d*. The number of databases is arbitrary, but each of them must be located in separate directory. The software has built-in utilities for data export and data export operations that provide possibility of data exchange among databases.

HOW TO USE THE SOFTWARE PACKAGE

Conventional Signs:

One should use the following signs for typing characteristic function (e.g. Gibbs energy) expressions:

x – mole fraction (in binary A-B systems it is mole fraction of B);

T – temperature, K;

p – pressure, bar;

R – gas constant (8.31451 J/(mole*K));

Sid = $-R*(x*\ln(x) + (1-x)*\ln(1-x))$ – mole entropy of formation of an ideal solution.

The program does not distinguish small and capital letters, in other words the program equally treats *t* and *T*, *p* and *P*, *Sid* and *sid*, etc.

The syntax of the characteristic function expressions is similar to that of Basic programming language. Admissible operators include: +, -, *, / - addition, subtraction, multiplication and division respectively, ^ - raising to power (e.g. raising 2 to power 4.3 may be written as 2^4.3 or 2^(4.3)), **ln** – natural logarithm (e.g. ln(3.14)), **exp** – exponent (e.g. exp(7.23)).

In order to use the function defined as stability parameter, which is named as **function_name** in corresponding table, one should use the following syntax: ({function_name}).

General View, Destination of Windows and Buttons

The general appearance of the main window is shown on Fig.1. There are menu in the upper part of the window the main items of which are reviewed below.

Database

Open – change database,

Save – save all changes in database,

Create – create new database,

Close – quit the program.

Stability parameter – open the window Stability Parameters.

Mosaic diagram color – is used to change the color of mosaic diagram.

System

Save to file – download all information on active system into one file (with an extension *ter*), is used for data exchange,









Upload from file – upload the information on thermodynamic system from the data file (with an extension *ter*),

Save as text – download all information on active system into the text file.

Experimental data – type the experimental points that will be displayed at the phase diagram.

There is the table “Systems” that contains the list of systems in database ordered by alphabet. The empty field located below the table “Systems” serves for quick search of the system.

There are some specific buttons for data manipulation:

-  - go to the first item,
-  - go to previous item,
-  - go to next item,
-  - go to the last item,
-  - add new item,
-  - delete current item,
-  - fix active modifications,
-  - cancel active modifications.

The right part of main window contains four windows: “Comments”, “List of designations”, “Phases” and “Gibbs energy expression”. The two first windows are visible only if the boxes “Comments” and “Designations” in group “Display windows” are checked.

The window “Comments” may be used for various memos. The text written here is not used in calculations. In the database that is supplied with the program this field contains information on data source and some additional information.

The window “List of designations” is used to change some default settings of the program. For example it is possible to define new variable, say **a=123.456**, which may be used later in all expressions for given system. It is also possible to define here X interval using syntax **#xmin=...**, **#xmax=...**. In this case the program will compute diagram only for this interval. Sometimes it is necessary to change captions at the axes of phase diagram. One of the ways to it is to add the following text in “List of designations”: **#xcap=TEXT1**, **#ycap=TEXT2**. In this case captions on horizontal and vertical axes of the phase diagram will be replaced by TEXT1 and TEXT2 respectively.

The window “Phases” contains the list of all phases that form active system.

The window “Gibbs energy expression” is used for the input of analytical expressions of characteristic functions of the phase. If the expression is too long one can use dots (...) as a hyphen. There are also three additional fields in this window: “Tmin”, “Tmax” and “X”. The last one (X) is used to define the stoichiometric substance; value of X specifies the mole fraction of second component (B). Tmin and Tmax define the temperature interval for Gibbs energy expression. Each phase can have arbitrary number of Gibbs energy expressions defined for not overlapping temperature intervals. The ordinal number of current expression and total amount of them are displayed in the lower part of the window (e.g. 2/3 means that the second expression of 3 available is displayed).

As it was already mentioned the software provides possibility to use the table of built-in functions in Gibbs energy expressions. This feature is convenient when one function is used in expressions for many systems, e.g. stability parameters of phases, which are defined by the nature of components. To that aim instead of the fragment of mathematical expression a program-readable reference is used: ({function_name}). For example the expression $(1-x)*(\{\text{Mn_HCPA3-BCCA12}\})-T*\text{Sid}+x*(1-x)*30000$ describes the Gibbs energy of HCP phase of Mn-Sc system ($T = 300 - 1873\text{K}$). The two last items describe ideal and excessive function of mixing of solid solution while the expression ({Mn_HCPA3-BCCA12}) is the reference to the stability parameter of HCP phase of manganese provides the phase Mn(BCC_A12) is selected as base level.

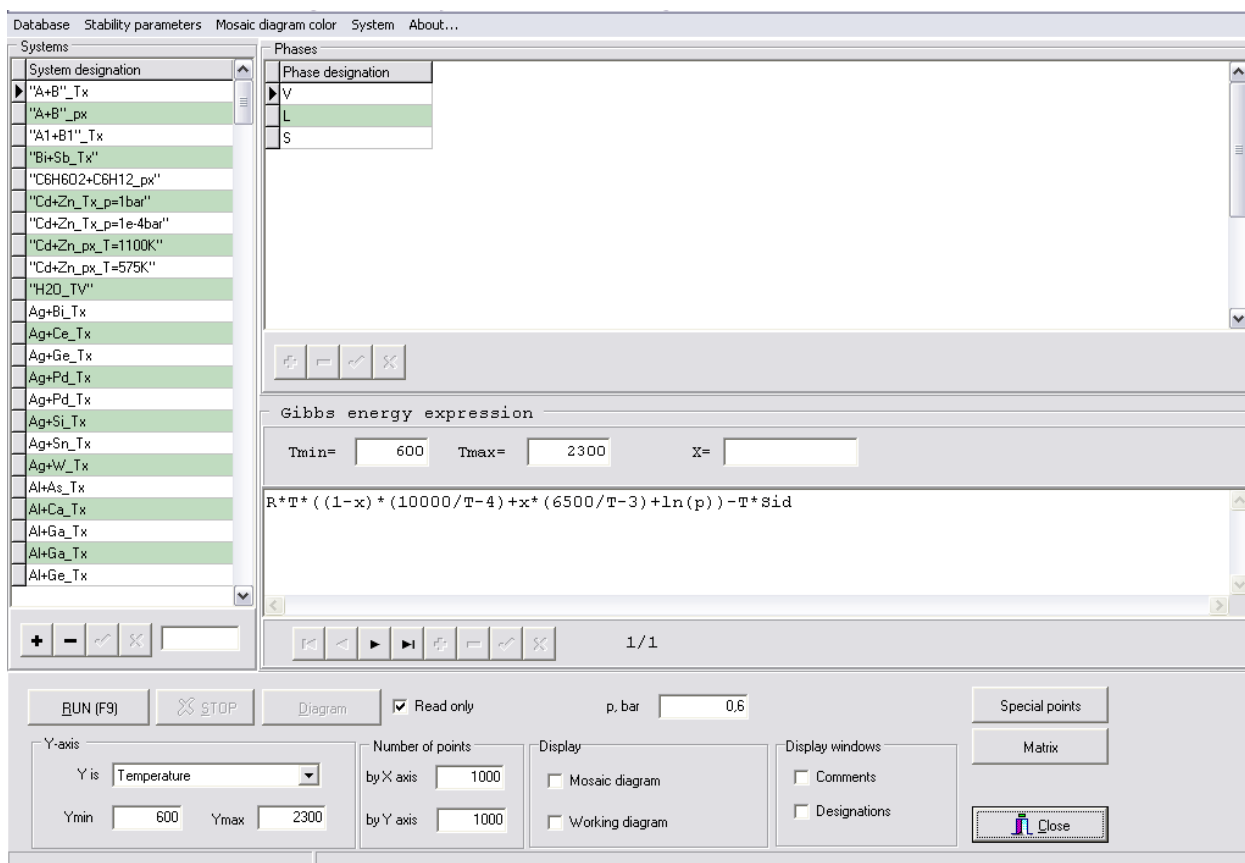


Fig. 1. General view of the main window

It is possible to view or modify the contents of the table of built-in functions using menu item “Stability parameter”. The general appearance of the window “Stability parameters” is shown on Fig. 2. The structure of the window and destination of control buttons are similar to these of the main window. Column “Designation” contains the list of function names.

We have used the following naming conventions. The function named as “(Element symbol|(Substance formula)_ phase” (e.g. As_G), describes the Gibbs energy of corresponding phase and element (or substance) in definite reference state at 298.15 K: $G-H_{SER}$ (SER – Standard Reference State), in this case of gaseous monatomic arsenic. The stable state of element (substance) is accepted as standard state at pressure 1 bar.

Such names like “(Element symbol|(Substance formula)_phase1-phase2” (e.g. Al_HCPA3-FCCA1) correspond to difference of Gibbs energies of phases 1 and 2 of the element or substance (e.g. $g_{Al}^{HCPA3} - g_{Al}^{FCCA1}$). This difference is stability parameter of the first phase (Al_HCPA3) provides the Gibbs energy of the second phase (Al_FCCA1) is selected as the base level. As a rule phases 2 are standard for corresponding conditions.

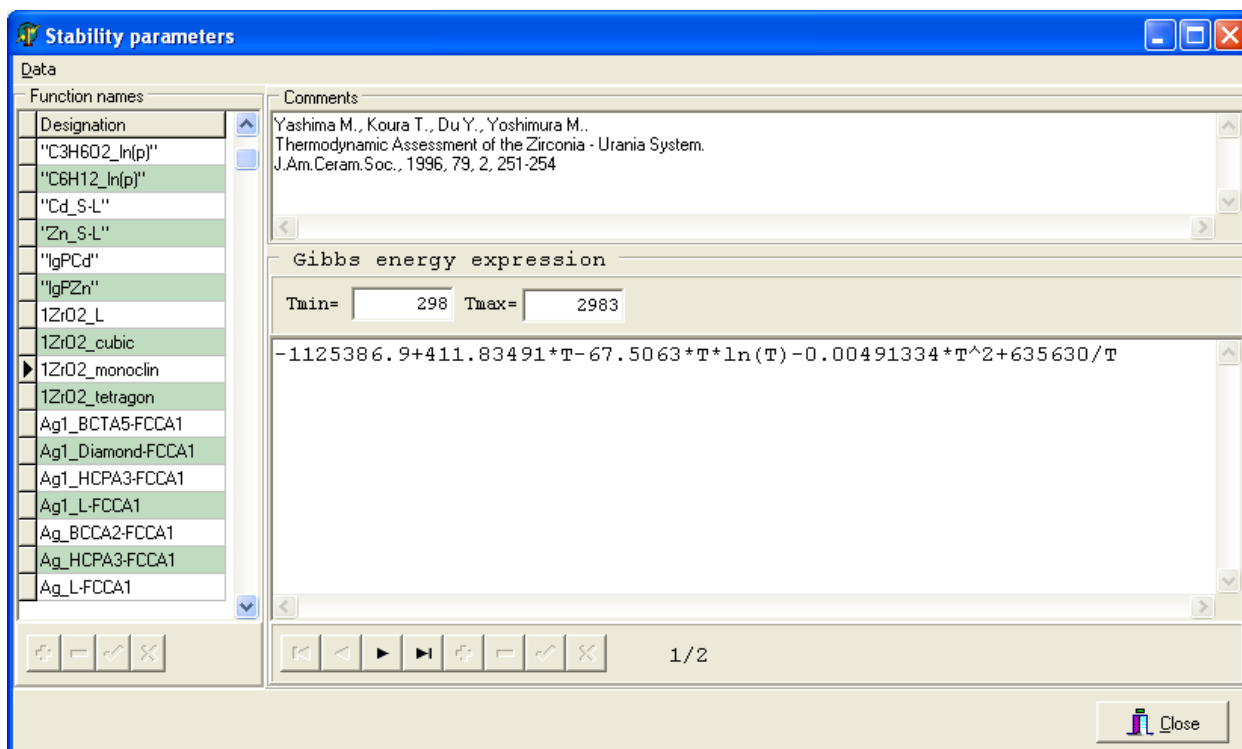


Fig. 2. General view of the window “Stability parameters”

The button “Run (F9)” is used to start the calculation of phase diagram, Fig.1. The button “Stop” located to the right of it serves for termination of the calculation process.

Current value of Y parameter is indicated at the left bottom part of main window.

To prevent the data from accidental corruption the checkbox “Read only” was introduced. While it is checked the data modification is prohibited.

It is possible to choose the kind of diagram section and set the interval of varied parameter in panel “Y-axis”. The value of fixed parameter (pressure or temperature) is set in the field located above the group “Display”. The panel “Number of points” contains the fields for the input of numbers in which Gibbs energy values of phases will be computed in calculation process. The more is the number the higher is accuracy calculation. But the time of calculation depends on the number of points too.

We can recommend the following combinations of numbers of points for X and Y axis: 50x50, 100x100, 200x200, 250x250, 400x400, 500x500, 800x800, 1000x1000 etc. One should better start from small number of points, raising the density of the grid points until the required accuracy is reached or computer resources exhausted. Sometimes the different numbers of points for X and Y axis is preferable. The best choice depends on specific of the system examined and on the quality of Gibbs energy functions $G(T, p, x)$ available. As a rule the general outline of phase diagram is achieved easily enough, but some of its fragments, such as some connodes or special points may disappear when the number of points is small, confer Fig.3 and Fig.4. In any case the computed diagram may be treated as good enough if significant change of the grid density used for calculation does not influence on the appearance of phase diagram. The accuracy of calculation of coordinates of phase equilibrium can be estimated from the value of interval between two neighbor points on each axis and the size of diagram by Y axis. E.g., if the grid 100x100 is used for the diagram in coordinates *Temperature-Composition* and the difference between T(max) and T(min) equals 1000K the uncertainty of phase diagram is not less than 0.5 mol percent by composition and 5K by temperature. It is evident the accuracy of calculations may be enhanced by reducing the Y interval (by decreasing the difference Ymax-Ymin).

In some cases the topological peculiarities of the phase diagram (such as very narrow area of existence of some phase) may cause errors in calculation of the diagram.

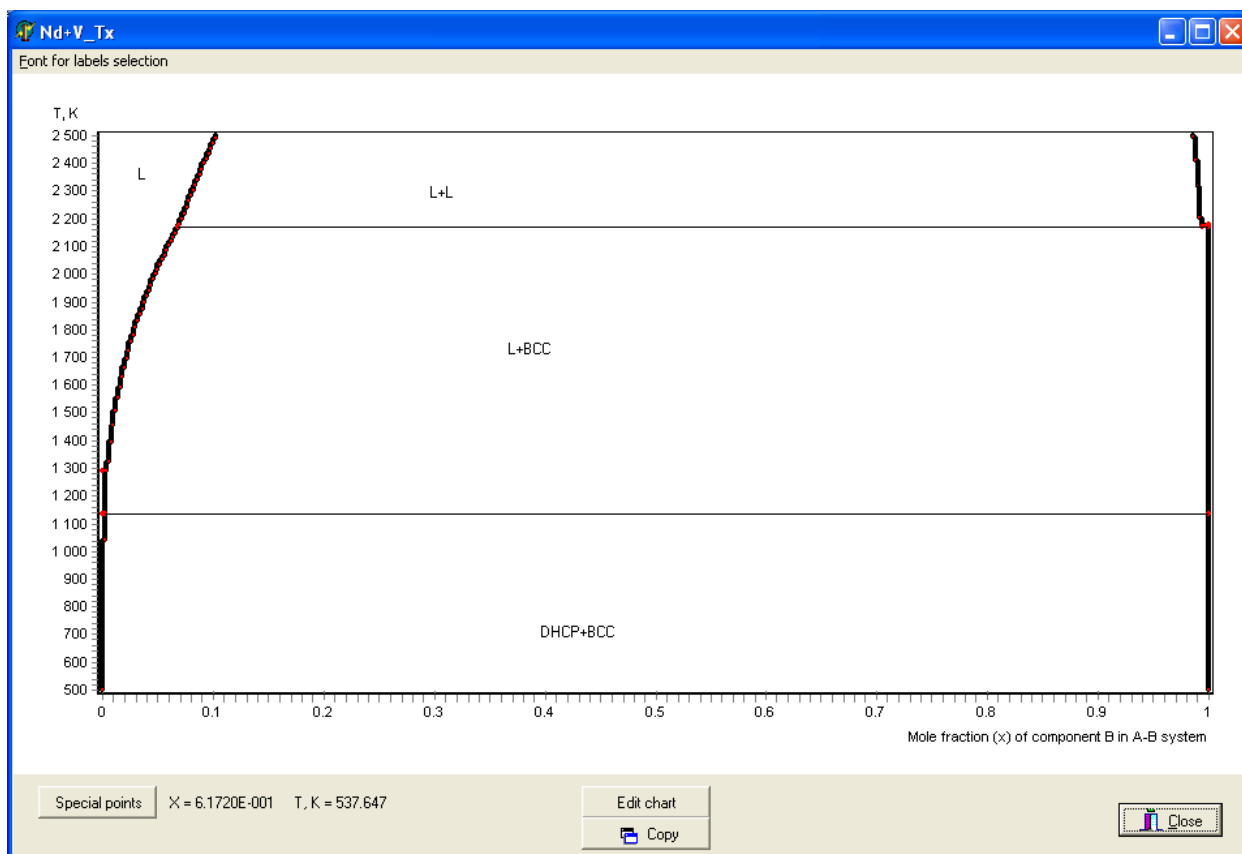


Fig. 3. Phase diagram of system Nd-V, calculation with the number of points 500x500

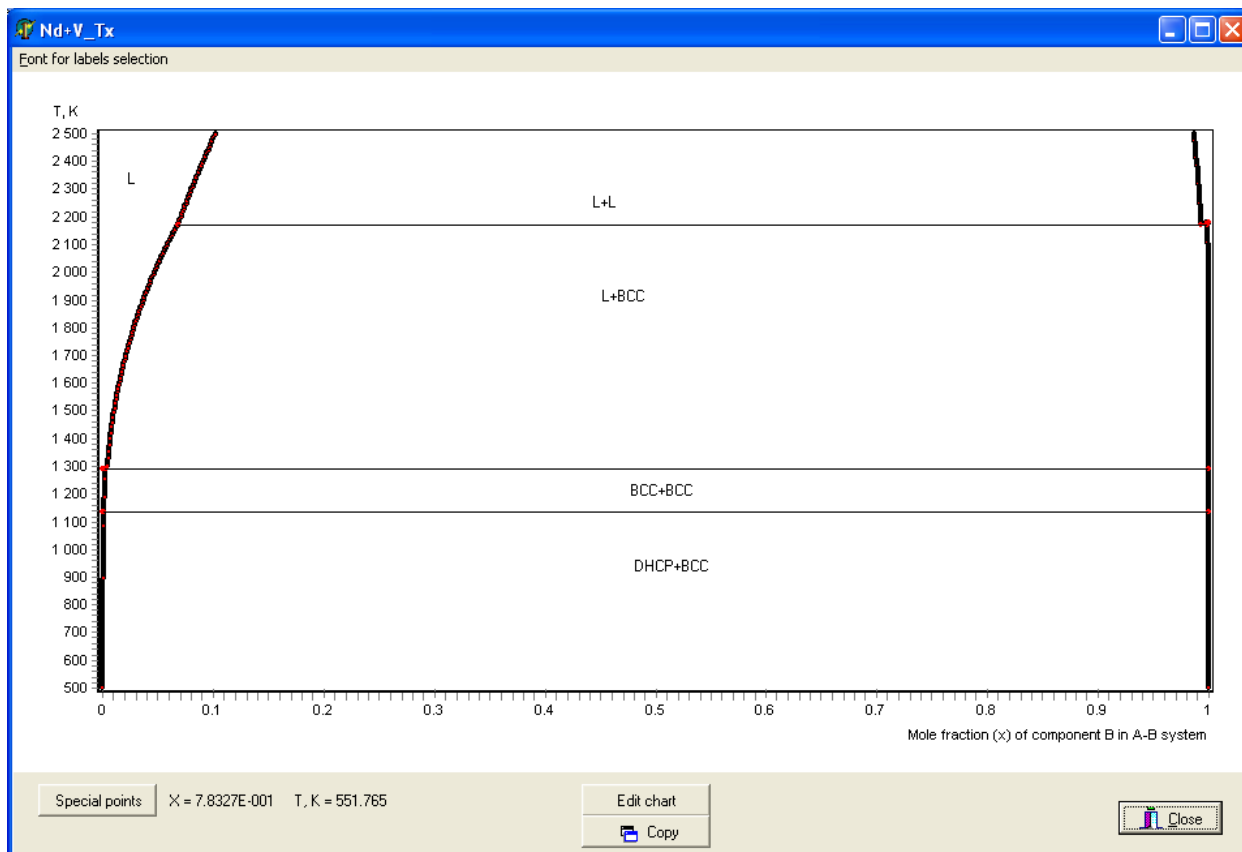


Fig. 4. Phase diagram of system Nd-V, calculation with the number of points 1500x500

When the diagram is computed and its graphical representation is ready the phase diagram window is displayed, Fig.5. The button “Diagram” in main window allows displaying this window if diagram is already computed.

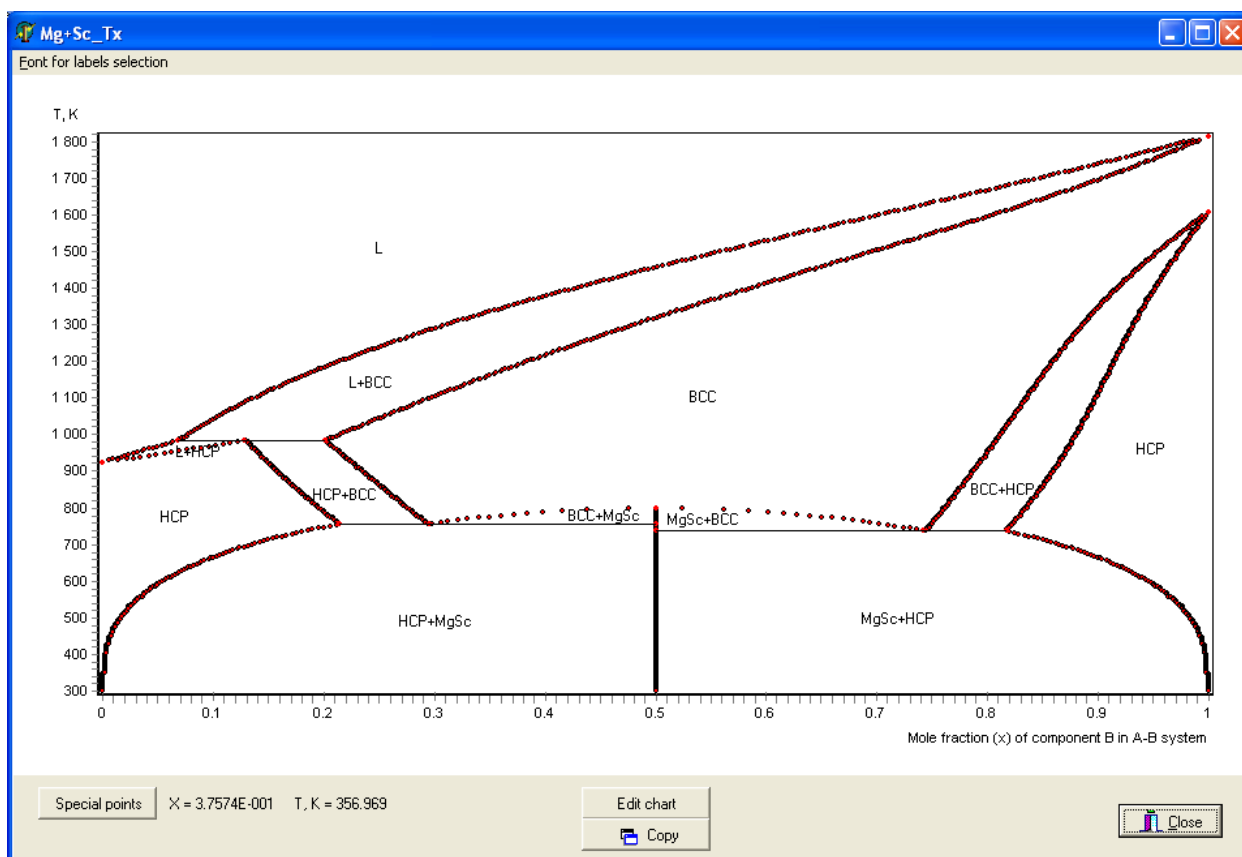


Fig. 5. Calculated (T_x) section of phase diagram for system Mg – Sc ($p = 1$ at)

Fields of the diagram may be marked by left mouse button click; phase names will correspond to these in list of phases. One can move the labels with phase names using left mouse button (standard drag-and-drop technique) or edit them using right mouse button. The cursor coordinates on phase diagram are displayed below the diagram.

Internal part of the chart (between the axes) may be moved to any direction by pressing right mouse button on it and mouse moving. The chart may also be zoomed by pressing left mouse button on upper left corner of the area and mouse moving to right and down direction. The appearing rectangle will define the zooming area. To restore the original chart press button “Undo Zoom”.

The bottom panel contains the button “Edit chart” pressing of which opens chart edit window, Fig.6.

The button “Special points” located to the left allows to display computed coordinates of special points of the phase diagram, Fig.7.

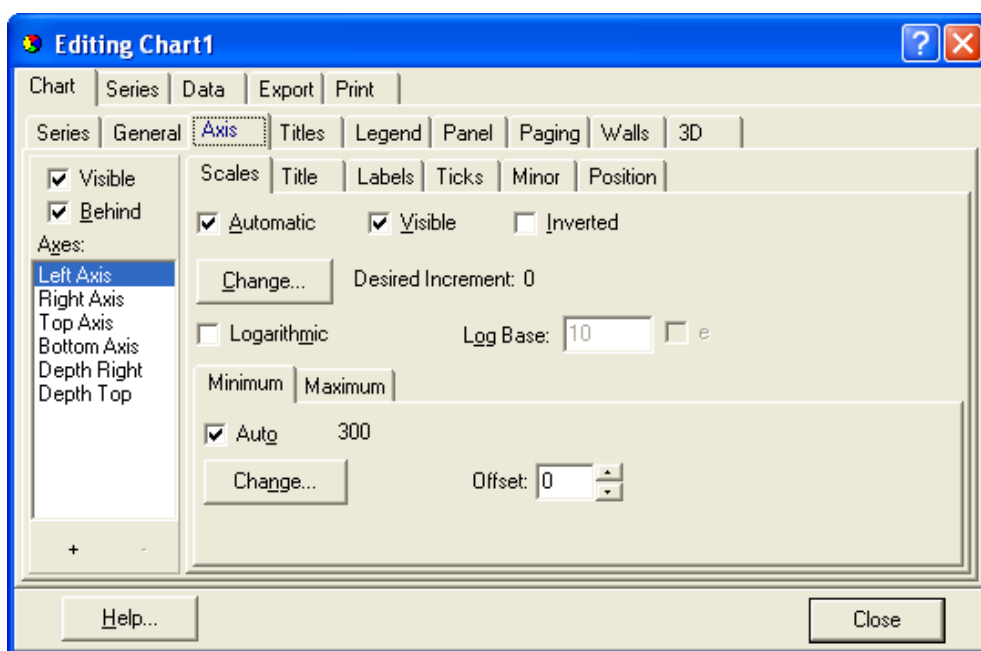


Fig. 6. Chart edit window

T	X(left)	X	X(right)
982.682	0.068	0.128	0.202
756.17	0.214	0.296	0.5
737.294	0.5	0.742	0.818

Other special points

$T(X = 1) = 1813.226$
 $T(X = 1) = 1605.59$
 $T(X = 0) = 924.481$
 $T(X = 0.5) = 797.068$

Close

Fig. 7. The window of special point coordinates

The software provides possibility to watch the dynamics of calculation process in two ways: via the convex hull and via the diagram itself, Fig.8. The left window displays Gibbs energies of phases (L, BCC, HCP) and their convex hull. The right window displays “shadow” of diagram. These windows will be seen if corresponding boxes in the group “Display” are checked.

During the calculation process the phase matrix is filled. To look at the matrix (that is indeed the skeleton of the diagram) one should press button “Matrix” in main window. Cells marked with yellow color correspond to heterogeneous fields and the cells of homogeneous area (white) contain the phase names, Fig.9.

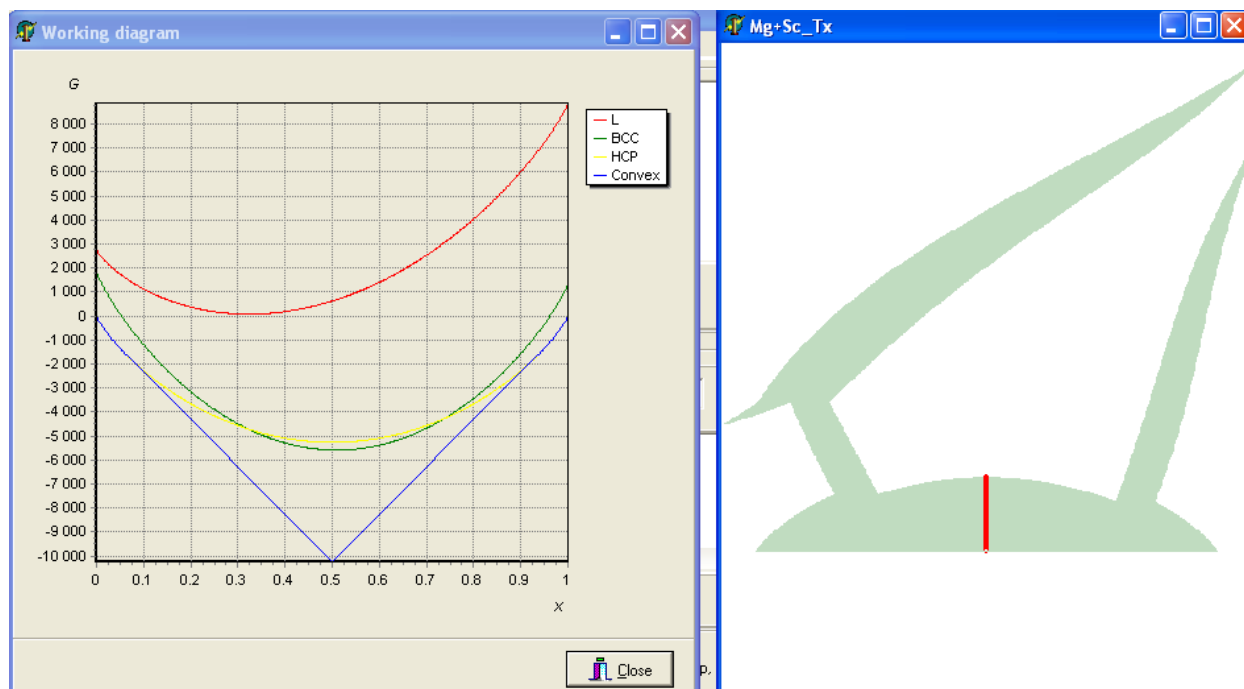


Fig. 8. The fragment of calculation of isobaric section, system Mg-Sc

Y/X	0.006	0.008	0.01	0.012	0.014	0.016	0.018	0.02	0.022	0.024
944.93	L	L	L	L	L	L	L	L	L	L
941.784	L	L	L	L	L	L	L	L	E	E
938.638	L	L	L	L	L	L	L	E	E	E
935.492	L	L	L	L	L	E	E	E	E	E
932.346	L	L	L	E	E	E	E	E	HCP	H
929.2	L	E	E	E	HCP	HCP	HCP	HCP	HCP	H
926.054	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	H
922.908	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	H
919.762	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	H
916.616	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	H
913.47	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	H
910.324	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	H
907.178	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	H
904.032	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	H
900.886	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	H
897.74	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	H
894.594	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	H
891.448	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	H
888.302	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	HCP	H

Fig. 9. Fragment of the matrix, system Mg-Sc

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Example 1. A – B Binary System

Construct isobaric and isothermal sections of the phase diagram of system A - B with isostructural solid solutions and absence of stoichiometric phases. The enthalpies of melting and temperatures of fusing are known: $T_m(A) = 1200$ K, $\Delta_m H_{1200}^0(A) = 12/R$ J/mol, $T_m(B) = 800$ K, $\Delta_m H_{800}^0(B) = 8/R$ J/mol. The temperature dependences of vapor pressure of pure component may be approximated

$$\ln p_A^s(\text{bar}) = -\frac{10000}{T} + 4$$

$$\ln p_B^s(\text{bar}) = -\frac{6500}{T} + 3$$

Solid and liquid solutions can be described by model of regular solutions with parameters 40 and 30 kJ/mol accordingly. The vapor can be considered as a mixture of ideal gases.

Method

Gibbs energies of mixing of condensed phases are known from conditions of a problem:

$$\begin{aligned}\Delta_{mix} g^s(T, x) (J/mol) &= g^s(T, x) - (1-x)g_A^s(T, x=0) - xg_B^s(T, x=1) = x(1-x)40000 - T \cdot s^{id} \\ \Delta_{mix} g^l(T, x) (J/mol) &= g^l(T, x) - (1-x)g_A^l(T, x=0) - xg_B^l(T, x=1) = x(1-x)30000 - T \cdot s^{id} \quad (\text{Ex1.1}) \\ \Delta_{mix} g^v(T, x) (J/mol) &= g^v(T, x) - (1-x)g_A^v(T, x=0) - xg_B^v(T, x=1) = -T \cdot s^{id}\end{aligned}$$

However equations (Ex1.1) cannot be used directly for calculation of the diagram because pure solid, liquid and gaseous component are chosen as reference state of Gibbs energies of solution for solid, melt and vapor phases accordingly. To unify the reference state, it is possible to add Gibbs energy of the pure components in select phase, for example, liquid to the right and left parts of equation (Ex1.1):

$$\begin{aligned}g^s + (1-x)(g_A^l - g_A^s) + x(g_B^l - g_B^s) &= x(1-x)40000 - T \cdot s^{id} + (1-x)g_A^l + xg_B^l \\ g^l + (1-x)(g_A^l - g_A^l) + x(g_B^l - g_B^l) &= g^l = x(1-x)40000 - T \cdot s^{id} + (1-x)g_A^l + xg_B^l \quad (\text{Ex1.2}) \\ g^v + (1-x)(g_A^l - g_A^v) + x(g_B^l - g_B^v) &= -T \cdot s^{id} + (1-x)g_A^l + xg_B^l\end{aligned}$$

Having rearranged last equations (Ex1.2), we receive expressions for Gibbs energies of all phases concerning a uniform reference state:

$$\begin{aligned}\Delta g^{s,ref}(T, x) &= g^s(T, x) - (1-x)g_A^l - xg_B^l = x(1-x)40000 - T \cdot s^{id} - (1-x)\Delta_m g_A - x\Delta_m g_B \\ \Delta g^{l,ref}(T, x) &= g^l(T, x) - (1-x)g_A^l - xg_B^l = x(1-x)40000 - T \cdot s^{id} \quad , \quad (\text{Ex1.3})\end{aligned}$$

$\Delta g^{v,ref}(T, x) = g^v(T, x) - (1-x)g_A^l - xg_B^l = -T \cdot s^{id} + (1-x)\Delta_v g_A + x\Delta_v g_B$
where $\Delta_m g_i = (g_i^l - g_i^s)$, $\Delta_v g_i = (g_i^v - g_i^l)$ are changes of Gibbs energy of melting and evaporation of components accordingly.

Thermodynamic characteristics of fusion of components can be defined from conditions of a problem. As at equilibrium melting $\Delta_m H_{T_m}^0 = T_m \Delta_m S_{T_m}^0$, so:

$$\Delta_m g_A = \frac{12}{R} - T \frac{12}{1200R} = \frac{12}{R}(1200 - T)$$

$$\Delta_m g_B = \frac{8}{R}(800 - T)$$
(Ex1.4)

Vapor is a mixture of ideal gases, so Gibbs energy of mixing of pure gaseous components may be expressed as $\Delta_{mix} g^v = -Ts^{id}$. Gibbs energies of evaporation of components can be defined from the vapor pressures of pure substances: $\Delta_v g_i^0 = -RT \ln p_i^s$.

The dependence of Gibbs energy from pressure (p is the total pressure in system in a bar, it is a parameter of calculation) is negligible in the case of condensed phases and should be considered for a gas.

As a result:

$$\Delta g^{s,ref}(T, x) = (1-x) \frac{12}{R} (T - 1200) + x \frac{8}{R} (T - 800) - T \cdot s^{id} + x(1-x)40000$$

$$\Delta g^{l,ref}(T, x) = -T \cdot s^{id} + x(1-x)30000$$

$$\Delta g^{v,ref}(T, x) = RT(1-x) \left(\frac{10000}{T} - 4 \right) + RTx \left(\frac{6500}{T} - 3 \right) - T \cdot s^{id} + RT \ln p$$
(Ex1.5)

According to (Ex1.5) next expressions should be written in a window " **Gibbs energy expression**" for calculation of the phase diagram:

$(1-x) \cdot 12/R \cdot (T-1200) + x \cdot 8/R \cdot (T-800) - T \cdot S^{id} + x \cdot (1-x) \cdot 40000$	for solid
$-T \cdot S^{id} + x \cdot (1-x) \cdot 30000$	for melt,
$R \cdot T \cdot ((1-x) \cdot (10000/T - 4) + x \cdot (6500/T - 3) + \ln(p)) - T \cdot S^{id}$	for vapor.

The result of calculations is shown at Fig. 10, 11. Figure 10 corresponds to next parameters of diagram: "Y" is temperature, Ymin = 600, Ymax = 2300, P=0.6, and Fig. 11 is produced if "Y" is a pressure, Ymin = 0.05, Ymax = 0.5, T = 1600 and 1000 points on X and Y axes.

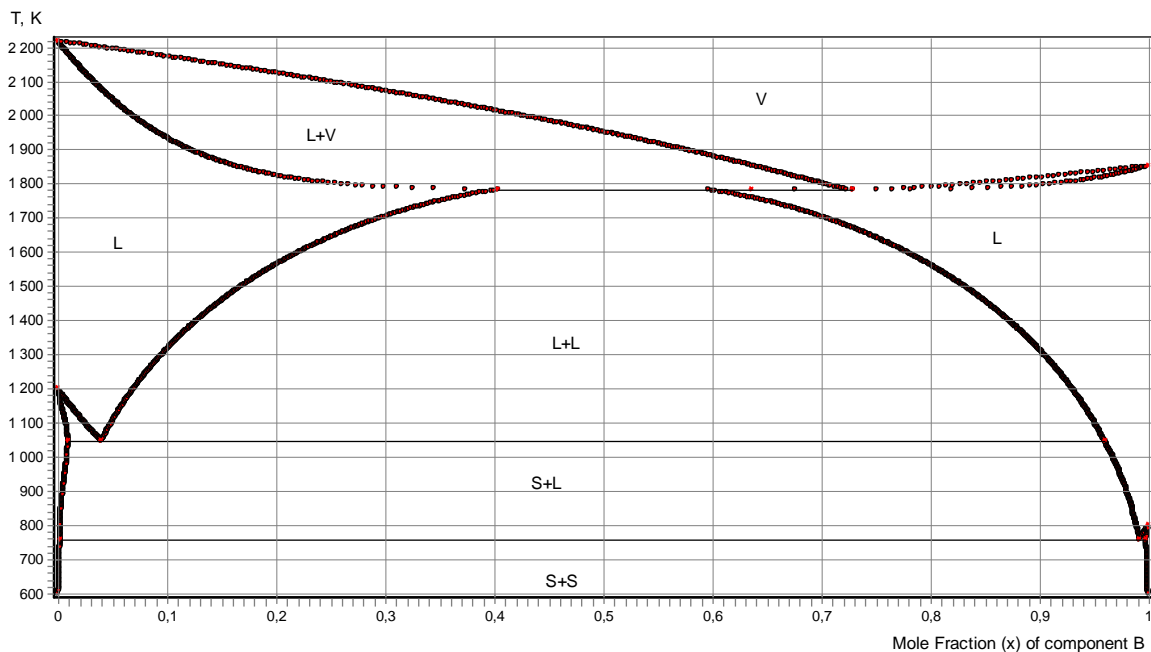


Fig. 10. Calculated (Tx) section of the A – B binary system phase diagram

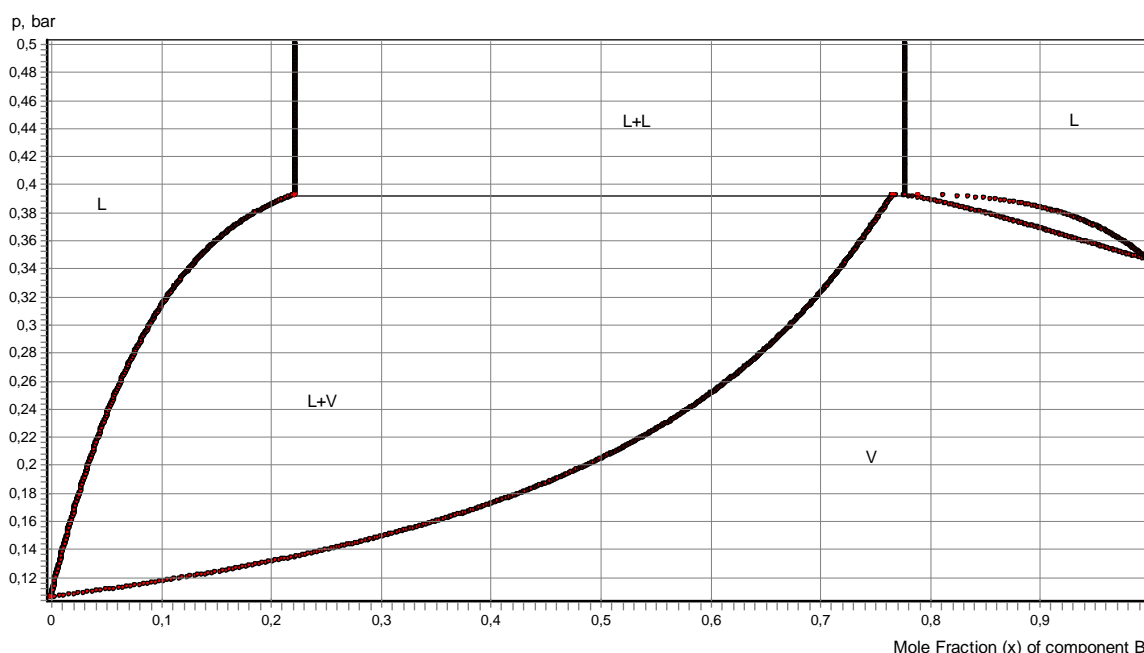


Fig. 11. Calculated (p_x) section of the A – B binary system phase diagram

Comments

The significance change of parameters of interaction g_0 in excess Gibbs energy of the condensed solutions results in receiving of various types of phase diagram. So, reduction g_0 of melt approximately in 3 times (from 30 up to 11 kJ/mol) leads to essential downturn of critical temperature of miscibility gap and to disappearance of azeotrope (Fig. 10, 12).

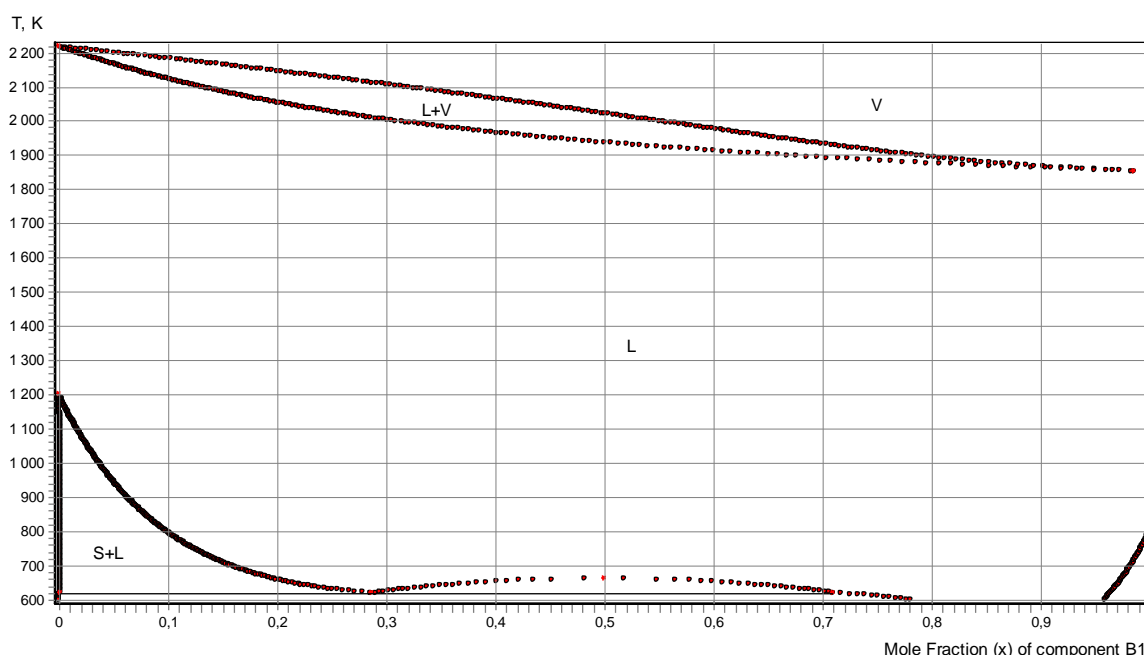


Fig. 12. Calculated (T_x) section of the A1 – B1 binary system phase diagram ($p = 0.6$ bar)

Example 2. Bi – Sb Binary System.

Construct the phase diagram of the Bi – Sb binary system at normal pressure in the solid and liquid solutions equilibrium field. It is known crystal bismuth, stibium and their solid solutions are isostructural and reference molar Gibbs energy alterations, caused solid (s) and liquid (l) solutions to form, may be described by quasiregular solutions formulas (Ex. 2.1, 2.2) when the temperatures are between melting points of the components.

$$\Delta_{mix} g^l(T, x) (\text{Дж} / \text{моль}) = x(1-x)(2228 - 2.3T) - T \cdot s^{id}, \quad (\text{Ex.2.1})$$

$$\Delta_{mix} g^s(T, x) (\text{Дж} / \text{моль}) = x(1-x)(6500 - 2.6T) - T \cdot s^{id}. \quad (\text{Ex.2.2})$$

Here $s^{id} = -R[x \ln x + (1-x) \ln(1-x)]$ – is the molar entropy of ideal solutions formation, x – mole fraction of Sb in the solution, R – universal gas constant ($8.31451 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$). Enthalpies and temperatures of bismuth and stibium melting are 11131 and 19875 J/mole, 544.6 and 903.7K³ accordingly.

Method

In the expressions in question solutions Gibbs energies, $g^l(T, x)$ and $g^s(T, x)$, have different count levels on account of the fact that reference system of comparison of solutions properties is founded on the corresponding properties of individual components, being in the same state (in the same phase) as the solution. That is,

$$g^l(T, x) - (1-x)g_{Bi}^l(T, 0) - xg_{Sb}^l(T, 1) = \Delta_{mix} g^l(T, x), \quad (\text{Ex.2.3})$$

$$g^s(T, x) - (1-x)g_{Bi}^s(T, 0) - xg_{Sb}^s(T, 1) = \Delta_{mix} g^s(T, x). \quad (\text{Ex.2.4})$$

By equilibria calculations Gibbs energies compared should be counted from unit level. So it is necessary to subtract addendum $(1-x)g_{Bi}^l(T, 0) + xg_{Sb}^l(T, 1)$ from both parts of (Ex.2.4) and present the equality in the following form:

$$g^s(T, x) - (1-x)g_{Bi}^l(T, 0) - xg_{Sb}^l(T, 1) = \Delta_{mix} g^s(T, x) - (1-x)\Delta_m g_{Bi}(T, 0) - x\Delta_m g_{Sb}(T, 1). \quad (\text{Ex.2.5})$$

Here $\Delta_m g_{Bi} = g_{Bi}^l - g_{Bi}^s$ – are Gibbs energy alterations been condition by pure components melting (at the temperature which in general case is not equal the temperature of their equilibrium melting). The functions $g^l(T, x)$ and $g^s(T, x)$ in the equations (Ex.2.3) и (Ex.2.5) have identical comparison system – individual liquid components to be in the same quantities as they are in the solutions.

For each of the components $\Delta_m g(T) = \Delta_m h(T) - T \cdot \Delta_m s(T)$, where $\Delta_m h$, $\Delta_m s$ and T_m – are molar enthalpy and entropy, and temperature of melting of the substance. Granted melting enthalpy and entropy do not depend on the temperature (the assumption is equivalent that one the heat capacity of the substance does not change during its melting), the written above data is sufficient (Ex.2.5) to evaluate Gibbs energy alteration are due to, in general case, not equilibrium melting of components, so far as $\Delta_m g(T) = \Delta_m s(T_m) \cdot (T_m - T)$ in according with the assumption in mind. So following expressions are to be written in the window «**Gibbs energy expression**» to construct the diagram:

$(2228 - 2.3 \cdot T) \cdot X \cdot (1 - X) - T \cdot \text{Sid}$ for melt,

$(6500 - 2.6 \cdot T) \cdot X \cdot (1 - X) - T \cdot \text{Sid} + \dots$

$(1 - X) \cdot (20.44 \cdot T - 11131) + X \cdot (21.99 \cdot T - 19875)$ for solid phase.

The result of the program work is presented at Fig. 13 (in the «Y» window should write temperature, **Ymin** = 110, **Ymax** = 910, **P** = 1 and 1000 points on X and Y axes).

³ М.А. Быков, Г.Ф. Воронин, Н.М. Мухамеджанова. *Прямые и обратные задачи химической термодинамики*. Новосибирск, «Наука», 1987, с.30

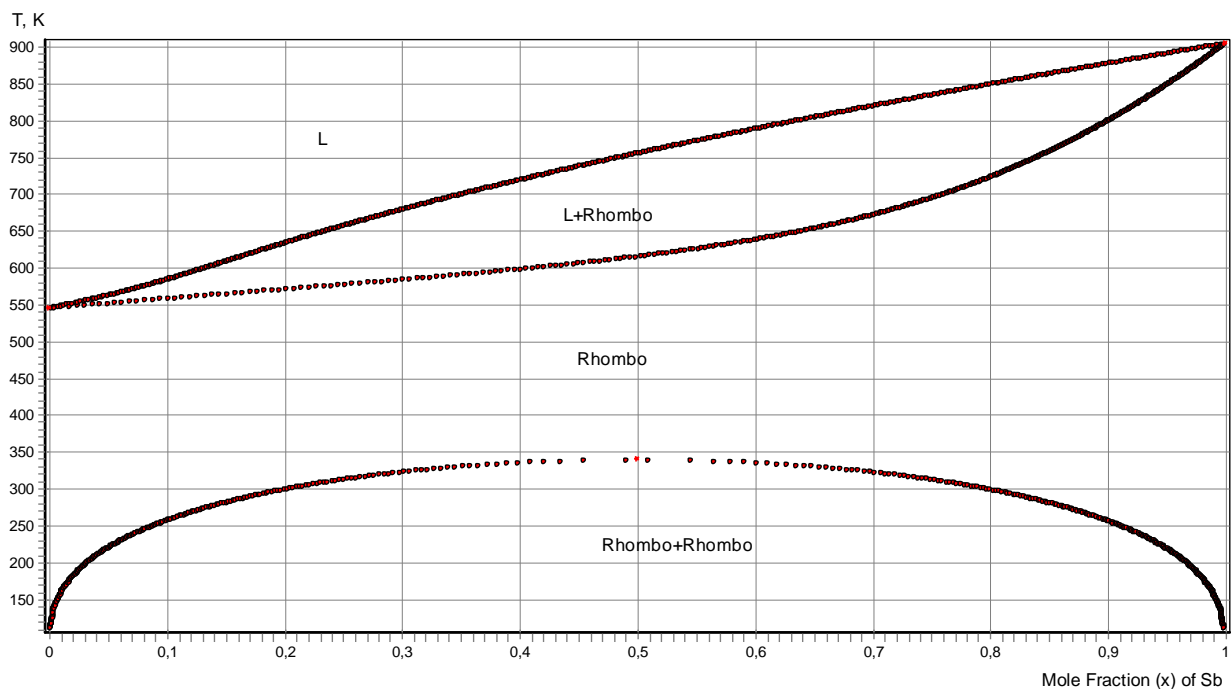


Fig. 13. Calculated (Tx) section of the Bi – Sb binary system phase diagram ($p = 1$ bar)

Comments

(a) Here the pressure p is assumed as an atmosphere one. However its value does not affect the result of calculations in present case owing to the expressions used do not contain this parameter. Such approach is usually used by calculation of the equilibria between condensed phases because their thermodynamic properties may be assumed not influenced by pressure at temperatures to lay far from the critical point and if pressures do not exceed several hundreds bar.

(b) Solid solutions stratification region submitted at the diagram disposes at very low temperatures. It is impossible to obtain sufficient reliable data relating to this area coordinates because of the fact that initial thermodynamic data concerns with the region of sufficiently high temperatures.

(c) Special points coordinates are 904.4, 544.4 and 338.0K at $x = 1, 0$ and 0.5 accordingly, i.e. accuracy of values of temperatures of the components melting, obtained by calculation, is not lower than 0.3K. The fact corresponds to the theoretical value of the permissible error of the temperature evaluation which is $(800/1000)/2=0.4$ K at $910 - 110 = 800$ K interval and 1000 points on Y axes.

Example 3. Cd – Zn Binary System.

Calculate isobaric and isothermal sections of the Cd – Zn binary system phase diagram. Three phases equilibria (crystal – components are isostructural, liquid and gas) must be taken into account. In accordance with⁴, molar Gibbs energy alterations of liquid and solid phases caused by their formation from liquid components may be presented as following expressions:

$$\begin{aligned} \Delta_{mix} g^l(T, x) (\text{Дж} / \text{моль}) &= x(1-x) [8780.20 - 0.21397T - x(1962.76 + 0.71608T) + x^2(2265.26 + 0.91875T)] - T \cdot s^{id}, \\ \Delta_{mix} g^s(T, x) (\text{Дж} / \text{моль}) &= x(1-x) [8560.86 - 11.67160T + x(13247.30 - 14.92080T)] - T \cdot s^{id} - \\ & (1-x)\Delta_m g_{Cd}(T, 0) - x\Delta_m g_{Zn}(T, 1), \end{aligned}$$

Here molar Gibbs energy alterations when components melted are:

⁴ Choi S.-D.A. Calphad, 1990, V.14, P. 307

$$\Delta_m g_{Cd} (\text{Дж} / \text{моль}) = 3948.4798 + 37.0186T + 0.0060794T^2 - 7.4015T \ln T,$$

$$\Delta_m g_{Zn} (\text{Дж} / \text{моль}) = 2827.9775 + 61.117T - 0.0062551T^2 + 41631/T - 10.6441T \ln T.$$

It is permitted to consider vapour phase as an ideal gas mixture formed by components atoms. To construct curves of vapour – condensed phases equilibrium one may use of expressions⁵ describing saturated vapour pressure of pure cadmium psCd and zinc psZn depend on the temperature from melting to vapouration points of individual components:

$$\ln p_{Cd}^s(\text{бар}) = -5908/T - 0.10076 \ln T - 0.000284T + 6.836, \quad T < 594.3K,$$

$$\ln p_{Cd}^s(\text{бар}) = -5819/T - 0.5459 \ln T + 9.406, \quad T \geq 594.3K,$$

$$\ln p_{Zn}^s(\text{бар}) = -6850/T - 0.3279 \ln T + 8.359, \quad T < 692.8K,$$

$$\ln p_{Zn}^s(\text{бар}) = -6620/T - 0.545 \ln T + 9.459, \quad T \geq 692.8K.$$

Method

In this task initial data size corresponds with one of the first example. The component vapour at 1 bar pressure may be taken for a reference state of the component of ideal gas mixture. To use of liquid components as a vapour properties count level one need to write (by analogy to (Ex1.5)):

$$\Delta g^{v,ref}(p, T, x) = g^v(p, T, x) - (1 - x^v) g_{Cd}^l(T, 0) - x^v g_{Zn}^l(T, 1) = \Delta_{mix} g^v(p, T, x) + (1 - x^v) \Delta_v g_{Cd}^0(T, 0) + x^v \Delta_v g_{Zn}^0(T, 1).$$

(Ex3.1)

Here x^v – is the Zn mole fraction in the vapour, $\Delta_v g_{Cd}^0 = g_{Cd}^{v,0} - g_{Cd}^{l,0}$ describe Gibbs energy (or $\Delta_v g_{Zn}^0 = g_{Zn}^{v,0} - g_{Zn}^{l,0}$ chemical potentials) alterations caused by pure liquid components vaporization at 1 bar pressure. This isothermal process may be considered as a two stage one: liquid vaporization to form vapour being in the equilibrium state concerning the liquid at saturated vapour pressure p_i^s , and subsequent expansion of the vapour in mind to reference value 1 bar. At the first stage chemical potentials of component being in liquid and vapour phases are equal and ideal vapour chemical potential alterations caused by vapour expansion from p_i^s to 1 bar pressure are equal to expansion-compression work $-RT \ln p_i^s$ correct to a sign. So it is possible to rewrite the equality written above in the following way:

$$\Delta g^{v,ref}(p, T, x^v) = \Delta_{mix} g^v - (1 - x^v) RT \ln p_{Cd}^s(\text{бар}) - x^v RT \ln p_{Zn}^s(\text{бар}). \quad (\text{Ex3.2})$$

To take account of the fact, that $\Delta_{mix} g_i^v = RT \ln p_i(\text{бар})$, the first addendum of the right side (Ex3.2) convert into the following form:

$$\Delta_{mix} g^v = (1 - x^v) RT \ln p_{Cd}(\text{бар}) + x^v RT \ln p_{Zn}(\text{бар}). \quad (\text{Ex3.3})$$

Here p_{Cd} and p_{Zn} – are components pressures in the vapour, which is in equilibrium state to the liquid solution having x composition (it is appropriate to pay attention to the fact that x and x^v are different in general case). It may be written $p_{Cd} = (1 - x^v)p$ for ideal gas mixture, where $p = p_{Cd} + p_{Zn}$ $p_{Zn} = x^v p$

⁵ О. Кубашевский, С.Б. Олкокк. *Металлургическая термехимия*. М., Metallurgia, 1982, 392 С.

– is the general pressure in the system, which has been given. The following expression can be obtained as a result:

$$\Delta g^{v,ref}(p, T, x^v) / RT = \ln p - (1 - x^v) \ln p_{Cd}^s(bar) - x^v \ln p_{Zn}^s(bar) - s^{id} / R. \quad (Ex3.4)$$

When phase diagram constructed any phases equilibrium curves must be drawn in the unit coordinates and x^v should be replaced by x in the formulas mentioned above. So following expressions should be written in the program work window:

$$x*(1-x)*(8780.20-0.21397*t-(1962.76+0.71608*t)*x+(2265.26+0.91875*t)*x^2)-t*Sid - \text{melt},$$

$$x*(1-x)*(8560.86+11.67160*t+(13247.30-14.92080*t)*x)+... \\ (1-x)*(\{\text{"Cd_S-L"}\})+x*(\{\text{"Zn_S-L"}\})-t*Sid \quad - \text{solid},$$

$$R*T*(\ln(p)-2.30258*((1-x)*(\{\text{"lgPCd"}\})+x*(\{\text{"lgPZn"}\}))-t*Sid \quad - \text{vapour}.$$

There is some references to the program functions in the expressions written above: ($\{\text{"Cd_S-L"}\}$), ($\{\text{"Zn_S-L"}\}$), ($\{\text{"lgPCd"}\}$), ($\{\text{"lgPZn"}\}$). The first two are correspond with stability details of cadmium and zinc solid phases when the melt Gibbs energy has been chosen as a count level. The rest describe pressure – temperature dependence for components. This four functions need to be written in the table «*Stability parameters*»:

$-3948.4798-37.0186*T-6.0794e-3*T^2+7.4015*T*\ln(T)$	– “Cd_S-L”,
$-2827.9775-61.117*T-6.2551e-3*T^2-41631/T+10.6441*T*\ln(T)$	– “Zn_S-L”,
$(-5908/t-0.232*\ln(T)/2.30258-0.284e-3*T+6.836)$	– “lgPCd” ($T < 594.3K$),
$(-5819/t-1.257*\ln(T)/2.30258+9.406)$	– “lgPCd” ($T \geq 594.3K$),
$(-6850/t-0.755*\ln(T)/2.30258+8.359)$	– “lgPZn” ($T < 692.8K$),
$(-6620/t-1.255*\ln(T)/2.30258+9.459)$	– “lgPZn” ($T \geq 692.8K$).

There are constructed (Tx) sections of the diagram at $p = 1$ and 0.0001 bar at Fig. 14 – 15. Calculated normal boiling points of Cd and Zn are at temperatures 1036 и 1181K.

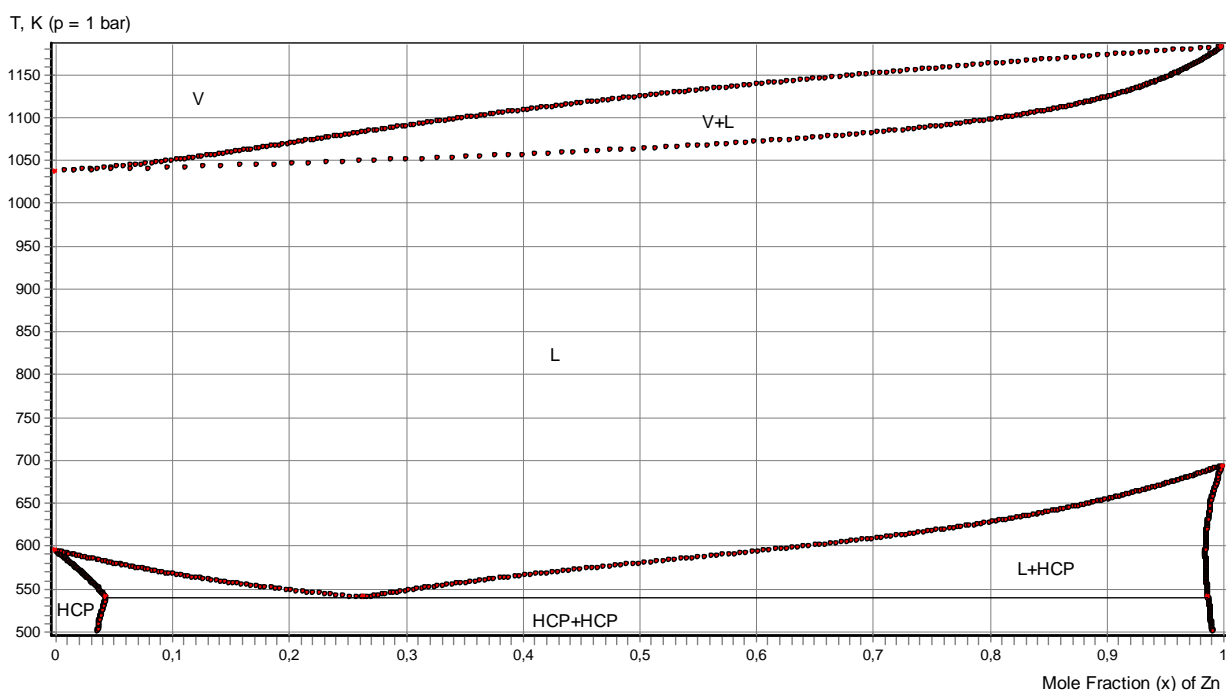


Fig. 14. Calculated (T_x) section of the Cd – Zn binary system phase diagram ($p = 1$ bar)

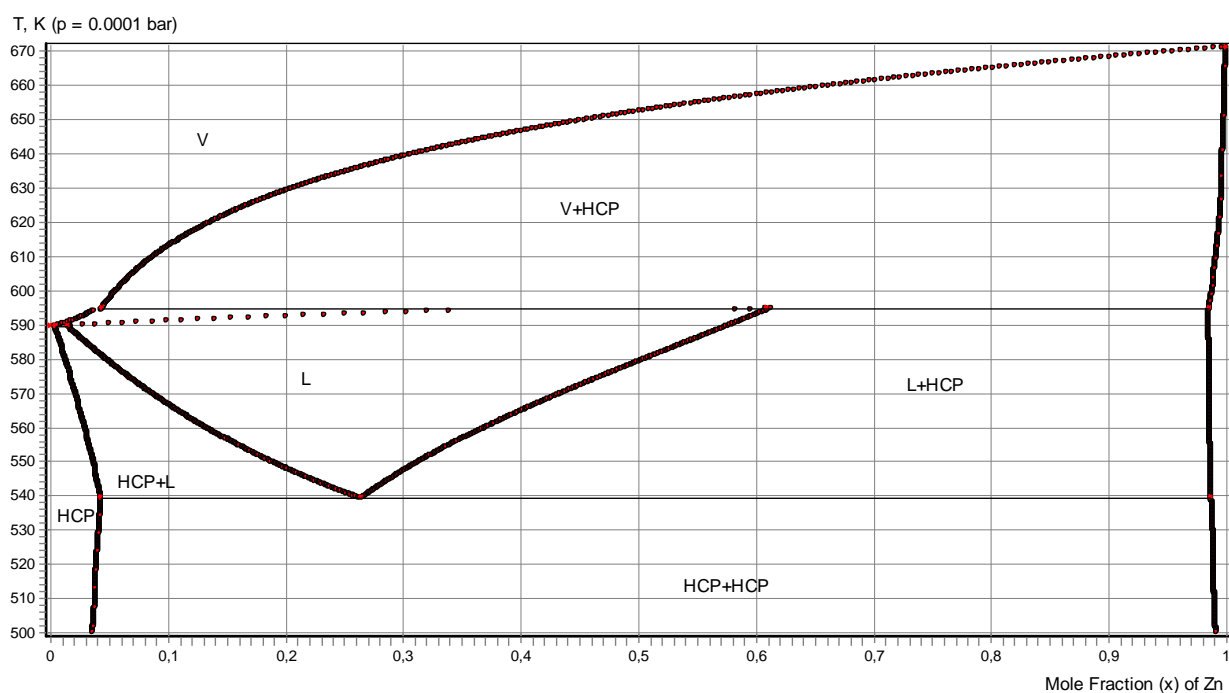


Fig. 15 Calculated (T_x) section of the Cd – Zn binary system phase diagram ($p = 0.0001$ bar)

The results of evaluations of pressure – composition diagrams at fixed temperatures 1100 and 575K are presented at Fig. 16 – 17.

Comments

(a) A little amounts diatom molecules Zn_2 , Cd_2 has been found in the Cd and Zn vapour mass-spectra side by side their atoms. Ideal associated gas model allows to calculate vapour curves at the phase diagram when atom association took into account.

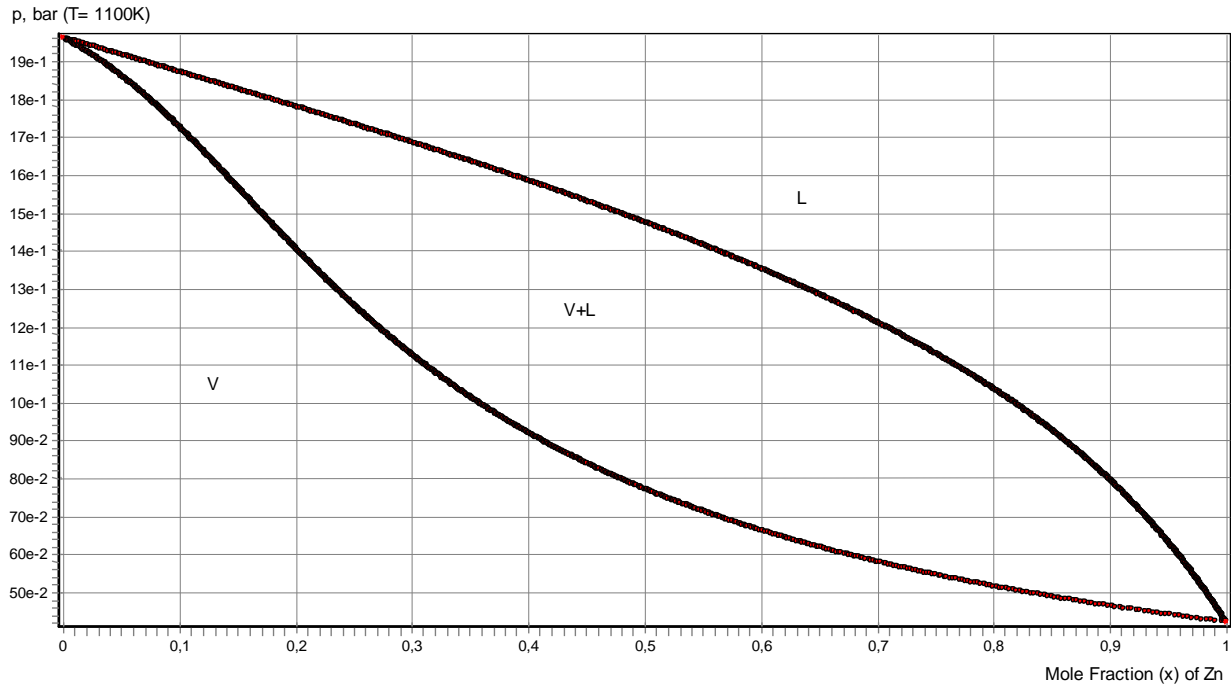


Fig. 16. Calculated (px) section of the Cd – Zn binary system phase diagram ($T = 1100\text{K}$)

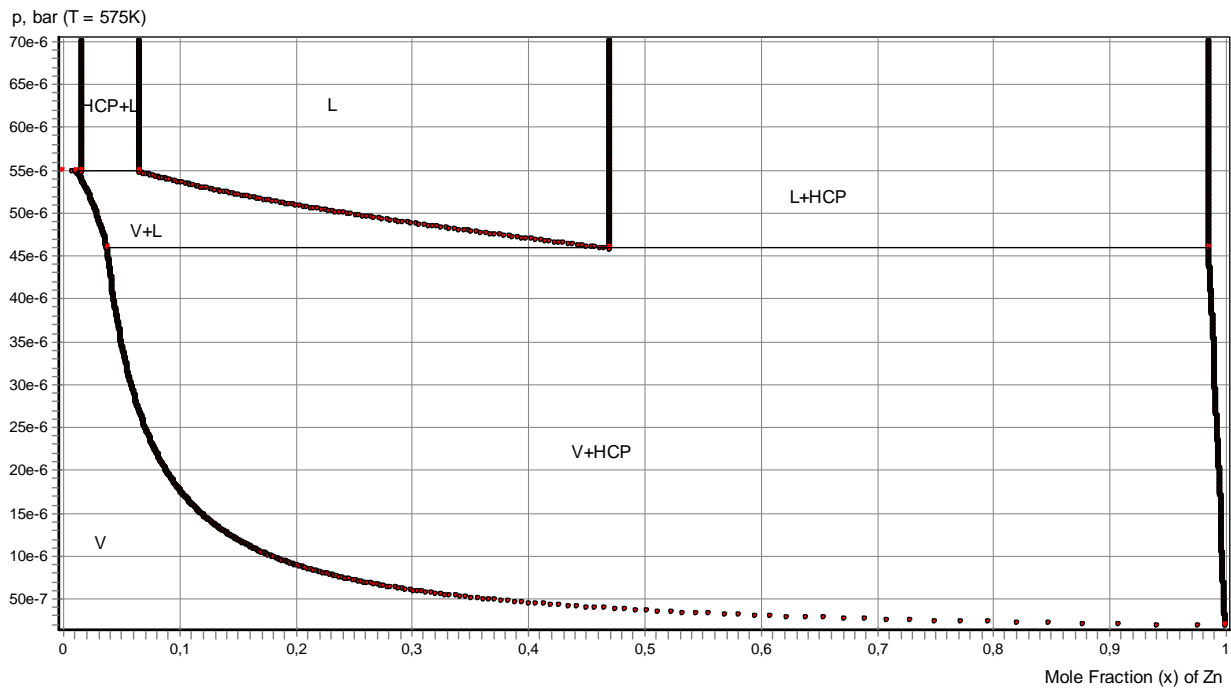


Fig. 17. Calculated (px) section of the Cd – Zn binary system phase diagram ($T = 575\text{K}$)

Example 4. Van-der-Vaalse Fluid

Construct a diagram describing liquid and gas phases equilibrium temperature of water and molar volume of fluid dependence not far from critical point. Van-der-Vaalse state equation

$p = \frac{RT}{V-b} - \frac{a}{V^2}$ (here V – fluid molar volume, a and b – numerical parameters) should be use of. $a = 5.468 \cdot 10^6 \text{ bar} (\text{sm}^3/\text{mole})^2$, and $b = 30.52 \text{ sm}^3/\text{mole}$ for water.

Method

The function $F(V) = F^0(T) - \frac{a}{V} - RT \ln(V-b)$ (here $F^0(T)$ does not depend on volume) may be obtained by integration of the expression describing isothermal alterations of Helmholtz energy,

$dF = -pdV$. During the integration it is necessary to use of mentioned above expression:
 $p = \frac{RT}{V-b} - \frac{a}{V^2}$. To find molar volumes of equilibrium phases at each definite temperature the program construct convex hulls of $F(V)$. Totality of data obtained at different temperatures brings about the task is solve. If the lower value of x axes $V_{\min} = 42$, and the highest $V_{\max} = 142 \text{ sm}^3/\text{mole}$ is chosen, and $R = 82.055 \text{ sm}^3 \cdot \text{bar} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$, following expression $F(V) - F^0(T)$ may be written in the program working window:

$$-5.468e6/x - 82.055 \cdot T \cdot \ln(x-30.52)$$

To edit X axes range it should be written in the window «*Mean*»:

```
#xmin=42
#xmax=142
```

The result of the program work are presented at Fig. 18.

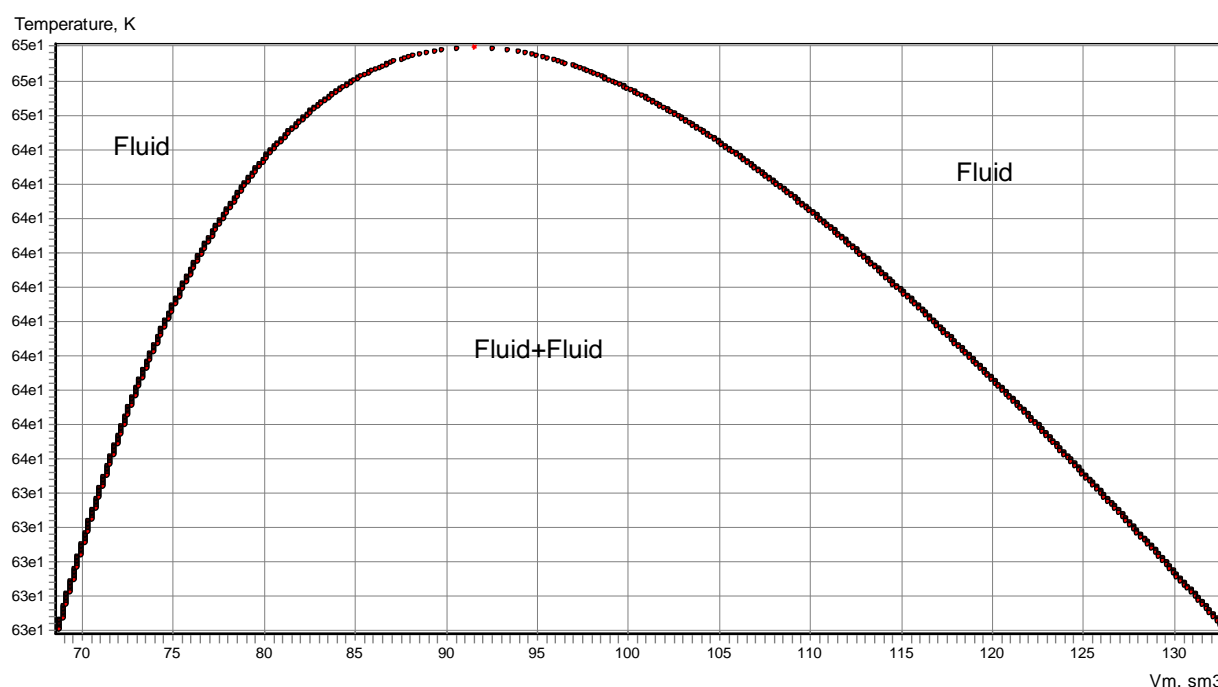


Fig. 18. Calculated (TV) section of the phase diagram of water

Comments

Calculated critical temperature 646.95K confirms experimental value 647.3K not bad. However critical volume, 92 sm3/mole, differs from experimental value (56 sm3/mole) sufficiently. The fact results from that, state equation chosen to evaluation is approximate one.

Example 5. Methyl-Acetate – Cyclohexane Binary System

Construct isothermal section of the methyl-acetate – cyclohexane binary system phase diagram in the range of vapour – melt equilibria. Gas phase may be considered as ideal gas mixture. Components saturated vapour pressure – temperature dependence⁶:

⁶ Polak, J.; Mertl, I., Saturated Vapour Pressure of Methyl Acetate, Ethyl Acetate, n-Propyl Acetate, Methyl Propionate, and Ethyl Propionate, Collect. Czech. Chem. Commun., 1965, 30, 3526-3528
 Williamham, C.B.; Taylor, W.J.; Pignocco, J.M.; Rossini, F.D., Vapour Pressures and Boiling Points of Some Paraffin, Alkylcyclopentane, Alkylcyclohexane, and Alkylbenzene Hydrocarbons, J. Res. Natl. Bur. Stand. (U.S.), 1945, 35, 219-244

$$\begin{aligned}\lg p^s(C_6H_6O_2) &= 4.20364 - \frac{1164.426}{T - 52.69}(\text{bar}) \quad T = 275 - 329K, \\ \lg p^s(C_6H_{12}) &= 3.96988 - \frac{1203.526}{T - 50.287}(\text{bar}) \quad T = 293 - 355K,\end{aligned}\quad (\text{Ex5.1})$$

and reference molar Gibbs energy alterations caused by liquid solutions formation at $T = 313K^7$:

$$\begin{aligned}\frac{\Delta_{mix}g^{0,l}}{RT}(x) &= -S_{id}/R + x(1-x)\left(\frac{a_1 \exp(ka_1)}{(1-x) + x \exp(ka_1)} + \frac{a_2 \exp(ka_2)}{x + (1-x) \exp(ka_2)}\right), \\ k &= k_1 + k_2(T - 273.15), \\ a_1 &= \frac{a_{11} + a_{12}(T - 273.15)}{RT}; \quad a_2 = \frac{a_{21} + a_{22}(T - 273.15)}{RT}, \\ k_1 &= -0.50277; \quad k_2 = -0.002106, \\ a_{11} &= 2953.6; \quad a_{12} = -14.53; \quad a_{21} = 3298; \quad a_{22} = -7.72(J/mole),\end{aligned}\quad (\text{Ex5.2})$$

is known. Here $s^{id} = -R[x \ln x + (1-x) \ln(1-x)]$ – is molar entropy of ideal solution formation, x – is cyclohexane mole fraction in the solution, R – universal gas constant ($8.31451 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$). In addition some points describing vapour pressure – solution composition dependence at 313K has been determined by experiment⁷ (x^l , x^v – are methyl-acetate mole fractions in melt and gas phase accordingly):

x^l	0.000	0.028	0.062	0.174	0.322	0.457	0.610	0.735	0.860	0.952	1.000
x^v	0.000	0.201	0.334	0.521	0.618	0.670	0.711	0.754	0.826	0.915	1.000
p , Pa	24623	29944	34730	46303	53302	56942	58422	59342	59222	56969	54062

Method

Melt and vapour are persistent solutions in the hole range of compositions $x = 0 - 1$ for this system. So temperature and composition dependence of Gibbs energy of the phases may be expressed as follows:

$$\begin{aligned}g^l &= (1-x) \cdot g_{C_3H_6O_2}^l(T, x=0) + x \cdot g_{C_6H_{12}}^l(T, x=1) + \Delta_{mix}g^l(T, x), \\ g^v &= (1-x) \cdot g_{C_3H_6O_2}^v(T, x=0) + x \cdot g_{C_6H_{12}}^v(T, x=1) + \Delta_{mix}g^v(T, x).\end{aligned}\quad (\text{Ex5.3})$$

To make sure unit count level of Gibbs energy of vapour and melt it is necessary to take pure components (being, for example, in liquid phase) Gibbs energy for referece state. Then:

$$\begin{aligned}\Delta g^{l,ref} &= \Delta_{mix}g^l(T, x), \\ \Delta g^{v,ref} &= (1-x) \cdot (g_{C_3H_6O_2}^{v,0}(T, x=0) - g_{C_3H_6O_2}^{l,0}(T, x=0)) + x \cdot (g_{C_6H_{12}}^{v,0}(T, x=1) - g_{C_6H_{12}}^{l,0}(T, x=1)) + \Delta_{mix}g^v(T, x).\end{aligned}\quad (\text{Ex5.4})$$

Value of reference Gibbs energy of liquids mixture at 313K $\Delta_{mix}g^{0,l}(x)$ is known from literature data and liquid phase Gibbs energy may be presented in a following way (it should be stressed that condensed phases properties depend on pressure very poorly at ambient conditions):

$$\frac{\Delta g_{313K}^{l,ref}}{313R}(x) = \frac{\Delta_{mix}g_{313K}^{0,l}}{313R}(x).\quad (\text{Ex5.5})$$

⁷ Int. Data Ser., Selec. Data Mixtures, Ser. A, 1975(1), 2-4

Right hand expressions (Ex5.5) – stability details – correspond to pure components vaporization at reference conditions. They may be determined when their saturated vapour pressure – temperature dependence treated:

$$\begin{aligned}
 g_{C_3H_6O_2}^{v,0}(T, x=0) - g_{C_3H_6O_2}^{l,0}(T, x=0) &= \Delta_v g_{C_3H_6O_2}^0(T, x=0) = -RT \ln \frac{p_{C_3H_6O_2}^s}{p^0} = \\
 &= -RT \cdot 2.303 \cdot \left(4.20364 - \frac{1164.426}{T - 52.69} \right), \\
 g_{C_6H_{12}}^{v,0}(T, x=1) - g_{C_6H_{12}}^{l,0}(T, x=1) &= \Delta_v g_{C_6H_{12}}^0(T, x=1) = -RT \ln \frac{p_{C_6H_{12}}^s}{p^0} = \\
 &= -RT \cdot 2.303 \cdot \left(3.96988 - \frac{1203.526}{T - 50.287} \right),
 \end{aligned}
 \tag{Ex5.6}$$

Here p^0, p_i^s – are reference and component saturated vapour pressures accordingly.

In accordance with task conditions vapour may be considered as ideal gas mixture. Then:

$$\Delta_{mix} g^v(T, x) = -T \cdot s^{id} + RT \ln p. \tag{Ex5.7}$$

Here p – is the total pressure above the system (see example 3).

To sum up Ex5.6 – Ex5.7, one may obtain the expression describing Gibbs energy of the gas phase:

$$\frac{\Delta g^{v,ref}}{RT}(T, p, x) = -(1-x) \cdot 2.303 \cdot \left(4.20364 - \frac{1164.426}{T - 52.69} \right) - x \cdot 2.303 \cdot \left(3.96988 - \frac{1203.526}{T - 50.287} \right) - s^{id} / R + \ln p. \tag{Ex5.8}$$

So to construct the phase diagram following expressions should be written (in accordance with Ex5.5 and Ex5.8) in the window «**Gibbs energy expression**»:

-Sid/R+x*(1-x)*((2953.6-14.53*(T-273.15))/R/T*exp((2953.6-14.53*(T-273.15))/R/T*(-0.50277-0.002106*(T-273.15)))/((1-x)+x*exp((2953.6-14.53*(T-273.15))/R/T*(-0.50277-0.002106*(T-273.15))))+(3298.1-7.72*(T-273.15))/R/T*exp((3298.1-7.72*(T-273.15))/R/T*(-0.50277-0.002106*(T-273.15)))/(x+(1-x)*exp((3298.1-7.72*(T-273.15))/R/T*(-0.50277-0.002106*(T-273.15)))))

melt,

-(1-x)*({"C3H6O2_ln(p)"})-x*({"C6H12_ln(p)"})-Sid/R+ln(p)

vapour,

and 2 functions – in « Stability parameters » table:

2.3*(4.20364-(1164.426/(T-52.69))) "C3H6O2_ln(p)",

2.3*(3.96988-1203.526/(T-50.287)) "C6H12_ln(p)".

To draw experimental points at the diagram it is necessary to choose «**Experimental points**» from «**System**» item and write down the data in the table (Fig. 19).

Experimental points				
Data source	Description X	X value	Description Y	Y value
▶	x(C6H12) in L	1	p, bar	0.243
		0.972		0.295
		0.938		0.343
		0.862		0.457
		0.678		0.526
		0.543		0.562
		0.39		0.577
		0.265		0.586
		0.14		0.584
		0.048		0.562
		0		0.533
	x(C6H12) in V	1		0.243
		0.799		0.295
		0.666		0.343
		0.479		0.457
		0.382		0.526
		0.33		0.562
		0.289		0.577
		0.246		0.586
		0.174		0.584
		0.085		0.562
		0		0.533

Fig. 19. The window to experimental data treatment

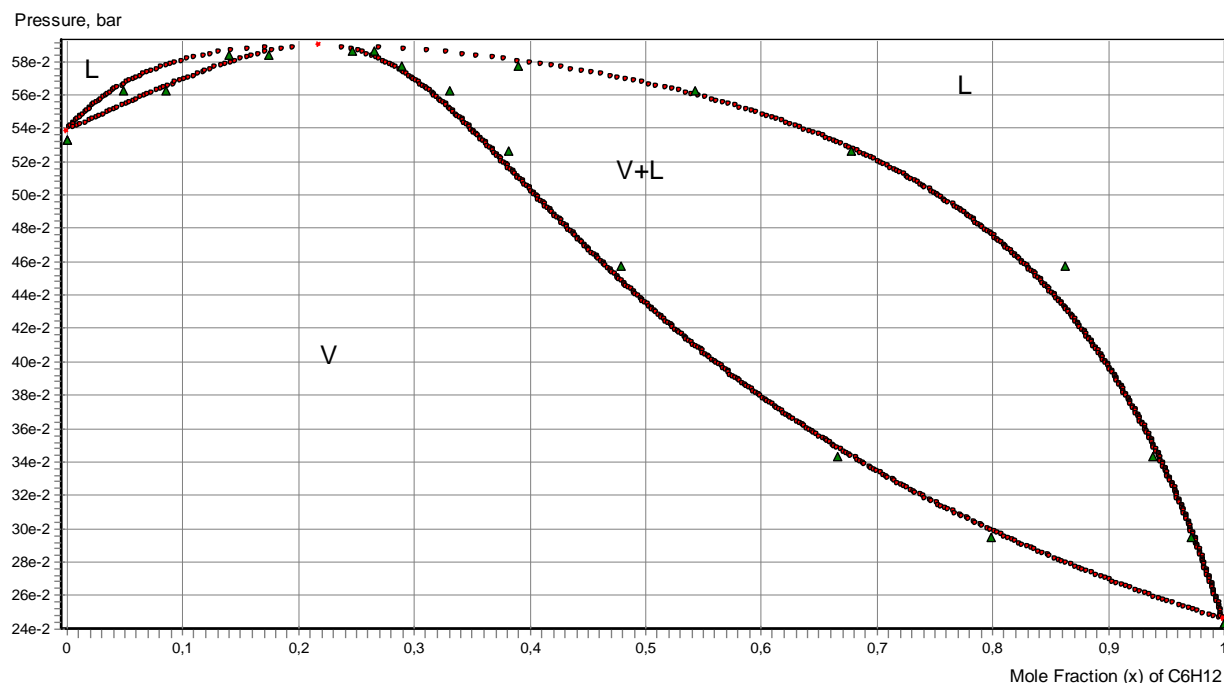


Fig. 20. Calculated (px) section of the $C_6H_6O_2 - C_6H_{12}$ binary system phase diagram

The results of the evaluation are presented at Fig. 20. Green triangles marks experimental points.

The software demo is accessible at the MSU Chemical Thermodynamic Lab. web-site:
<http://td.chem.msu.su/>