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PTGIBBS—an EXCEL™ Visual Basic program for computing and visualizing thermodynamic functions and equilibria of rock-forming minerals☆

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Abstract

PTGIBBS, a Visual Basic for Application program, was implemented in EXCEL™. It calculates mineral equilibria and thermodynamic functions for diverse solid solution phases, including presentation in 2D- and 3D-plots. The program is also suitable for the calibration and subsequent application of geothermobarometers, because of its ability to simultaneously calculate a large number of equilibria of the same type. Options are provided for the application of various equations of state (EOS). The volume behavior of mineral phases as a function of pressure can be expressed, e.g. by the Murnaghan EOS. It is also possible to model order–disorder transitions and lambda heat capacity anomalies using a tricritical Landau model including pressure dependence. Thus, PTGIBBS can be used with different thermodynamic data sets. It can handle molecular mixing models and mixing-on-site models with a maximum of nine components for each solid solution phase. An event-driven, interactive operating mode was selected for easy application of the program. Another advantage is the implementation in EXCEL™, resulting in a wide range of possible applications and the user-friendliness of PTGIBBS. The easy display of different thermodynamic functions and the simplicity with which input data sets can be changed may also be useful for teaching purposes.

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1. Introduction

During the last two decades, calculations of mineral equilibria on the basis of the laws of macroscopic thermodynamics, mainly to determine their *P*–*T* positions, have become an important tool for deciphering the *P*–*T* evolution of metamorphic rocks and the understanding of the underlying geodynamic processes. Various computer programs have been launched to undertake such calculations, often combined with a specific set of thermodynamic data that are, in some cases, internally consistent.

We concisely review these programs to outline why the computer program described here fills a gap within the frame of these computer programs related to mineral equilibria. Principally, we can distinguish between two types of programs. One type operates with fixed bulk rock compositions resulting, for instance, in the

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☆Code available from server at http://www.iamg.org/CGEditor/index.htm.

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calculation of so-called pseudosections (specific P–T diagrams—see Powell et al., 1998; Connolly and Petrini, 2002). The other type was mainly designed to determine mineral reaction curves for either pure phases or at least one participating phase with a fixed composition (or activity of a selected component in the corresponding phase) within a binary or multi-component solid solution series. The program package Ge0-Calc (Brown et al., 1988) involving PTX by Perkins et al. (1986) was one such type of program allowing computations with an extended internally consistent thermodynamic data set for 67 phases (Berman, 1988). Updates of this program package contained program and data sets for solid solution series (e.g. for garnet: Berman, 1990) to determine the activity of a mineral component in a phase as a function of P, T and X_1–X_n ($n \leqslant 6$). The results can also be integrated into a program for calculating reaction curves in a P–T space (e.g. Berman (1991): program TWQ).[1] An update also considers solid solution phases with $n \leqslant 8$.

The program package THERMOCALC[2] (Powell and Holland, 1988) was also able to determine the P–T position of mineral equilibria and invariant points in multi-component systems for diverse solid solution phases. This program also calculates the compositions of the solid solution phases at a selected invariant point (only indirectly possible with Ge0-Calc). Several updates of THERMOCALC with step-wise enlarged thermodynamic data sets were reported by Holland and Powell (e.g., 1990, 1998). The advantages of THERMOCALC over Ge0-Calc led to their use by several researchers to compute petrogenetic grids for diverse model systems (e.g., Na_2O–CaO–FeO–MgO–Al_2O_3–SiO_2–H_2O by Guiraud et al., 1990; K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O by Powell and Holland (1990); Klemd et al. (2002)), despite the non-user friendly input routine of THERMOCALC. Such grids were frequently applied to interprete the metamorphic evolution of rocks showing various types of protoliths (mainly metabasites and metapelites).

Similar to THERMOCALC, the program GIBBS[3] (Spear and Menard, 1989) was able to compute (step by step) petrogenetic grids, but with a thermodynamic data set for less mineral phases (or components) than Ge0-Calc and THERMOCALC. Various updates of GIBBS (e.g. by Spear et al. (1991): program PT-PATH) appeared in the literature. In a recent update, the data set by Holland and Powell (1998) was integrated. The original program GIBBS was also designed to calculate the variation of compositions of minerals, such as garnet, for fixed bulk rock compositions, also determining the modal variation of the rock. This was the first step in computing so-called pseudosections, which are P–T diagrams showing mineral reactions for a fixed bulk rock composition. An update version of GIBBS is now able to completely achieve this.

The program package THERIAK-DOMINO[4] started with the inclusion of a sub-routine for calculating mineral equilibria with complex non-ideal solid solutions (De Capitani and Brown, 1987). This sub-routine was also integrated by Berman (1991) in his program package (see above). THERIAK-DOMINO was updated several times and is now able to compute, for instance, pseudosections including the determination of an equilibrium assemblage at fixed P,T and bulk rock composition. The program package PERPLE_X,[5] launched by Connolly (1990), can compute such phase diagrams as well. After several updates, including the addition of the program VERTEXVIEW (Castelli et al., 1997), PERPLE_X is very capable in determining complex phase diagrams with various solid solutions.

This advantage is partially counteracted by complex input routines, which are hardly user-friendly and allow its use by only a limited number of scientists. These disadvantages of PERPLE_X can, to some degree, also be found in THERIAK-DOMINO, GIBBS and THERMOCALC. This may be the reason for the limited number of published examples of successful calculations of mineral equilibria from natural mineral assemblages. Ge0-Calc is, in fact, more user-friendly, but has significant limitations compared to the previously mentioned programs, for instance in the number of solid solution series and their components related to a specific mineral equilibrium. We see in the disadvantages of the above programs the reason that relatively simple computer programs were created to solve rather simple problems, such as the calculation of a single equilibrium for geothermobarometry (GPT by Reche and Martinez, 1996; EQMIN by Martin, 1996; PET by Dachs, 1998—although the latter also offers additional tools for calculating phase equilibria on the basis of the data sets by Holland and Powell (1990) and Berman (1988)). Thus, our aim was to create a user-friendly program package that is clearly more capable than GPT and EQMIN in order to determine the P–T positions of a large number of mineral equilibria with complex solid solution models. In this respect, we also enhanced the possibilities offered by Ge0-Calc. In addition, we considered the need of the metamorphic petrologist to undertake such calculations with numerous compositions of one or more minerals because of widespread

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[1] Software TWQ. http://www.gis.nrcan.gc.ca/twq.html.

[2] Software THERMOCALC. http://www.earthsci.unimelb.edu.au/tpg/thermocalc.

[3] Software GIBBS. http://ees2.geo.rpi.edu/MetaPetaRen/GibbsWeb/Gibbs1.html.

[4] Software THERIAK-DOMINO. http://titan.minpet.unibas.ch/base/bs.1uni.min/TheriakDomin.htm.

[5] Software PERPLE_X. http://www.perplex.ethz.ch/.

chemical zonations in minerals such as garnet and mica. Moreover, chemical data of minerals combined with estimated *P–T* conditions can be used to derive thermodynamic data for minerals and their solid solution properties. Our new program package PTGIBBS is suitable to support the geoscientist in doing this.

2. Basis of PTGIBBS

In order to provide a user-friendly computer program package for the metamorphic petrologist, we wanted to adapt it to a widespread computer program involving a flexible environment for processing data, extensive graphing capabilities for displaying data, and a high degree of compatibility with graphic and text processing computer programs. Therefore, we decided to use EXCEL™ by Microsoft® using the Microsoft® Windows operating system (e.g. Windows 98 to Windows XP). An advantage of this spreadsheet environment is the simplicity with which data can be changed, copied, selected and arranged. In addition, the large number of built-in functions (e.g. mathematical and statistical functions) enables the user to easily perform various kinds of calculations by developing individual worksheet applications. The clear tabular form represents a further advantage over the above mentioned programs, in which data sets are often complexly arranged in external files. The complex mineral equilibria calculations required are not readily handled within the structure of the grid cell calculations used by EXCEL™. In order to create a user-friendly, but also event-driven and interactive operating system in the EXCEL™ environment the powerful programming language "Visual Basic for Applications" (VBA) was used. By means of VBA, various thermodynamic calculation routines and functions could be adapted. Thus, the worksheets of PTGIBBS do not contain formulas, but it is possible to develop individual worksheet applications by means of the built-in thermodynamic functions.

3. Thermodynamic calculation procedure

In the following, we present the mathematical formulations which are part of the VBA built-in functions (see Table 1) and subroutines of PTGIBBS.

Table 1
Built-in thermodynamic functions in PTGIBBS. mfi = site (or mole) fraction of component *i* in a specific solid solution phase

Name of function	unit	Returns
aw_Get_mineral_index (phase_name)		Row index of phase in worksheet "mineral_data"
aw_Get_H0 (phase_name)	J	Standard state enthalpy of formation at 1 bar and 298.15 K
aw_Get_S0 (phase_name)	J/K	Standard molar entropy at 1 bar and 298.15 K
aw_Get_V0 (phase_name)	J/bar	Standard molar volume at 1 bar and 298.15 K
aw_volume_of_phase (*P*(bar), *T*(K), phase_name)	J/bar	Volume at *P* and *T*
aw_enthalpy_integral (*T*(K), phase_name)	J	Integral of $Cp\,dT$
aw_entropy_integral (*T*(K), phase_name)	J/K	Integral of $Cp/T\,dT$
aw_volume_Integral (*P*(bar), *T*(K), phase_name)	J	Integral of $V\,dP$
aw_Gtransition (*P*(bar), *T*(K), phase_name)	J	Gibbs energy of transition at *P* and *T*
aw_Gdisorder (*P*(bar), *T*(K), phase_name)	J	Gibbs energy of disorder at *P* and *T*
aw_GLandau (*P*(bar), *T*(K), phase_name)	J	Landau energy at *P* and *T*
aw_Gpure (*P*(bar), *T*(K), phase_name)	J	Gibbs free energy of a pure phase at *P* and *T*
aw_Gwater (*P*(kbar), *T*(K))	J	Gibbs free energy of water at *P* and *T*
aw_dG_reaction (*P*(bar) ,*T*(K), reaction_number)	J	Gibbs free energy of a reaction at *P* and *T*
aw_Gexcess (*P*(bar),*T*(K), phase_name,model_name, mf1,mf2,mf3,mf4,mf5,mf6,mf7,mf8,mf9)	J	Excess Gibbs energy of mixing of a phase component at *P* and *T*
aw_Gmix (P(bar),T(K), phase_name,model_name, mf1,mf2,mf3,mf4,mf5,mf6,mf7,mf8,mf9)	J	Gibbs energy of mixing of a phase component at *P* and *T*
aw_activity (P(bar),T(K), phase_name,model_name, mf1,mf2,mf3,mf4,mf5,mf6,mf7,mf8,mf9)		Activity of a phase component at *P* and *T*
aw_Gex_WH (phase_name, model_index, mf1,mf2,mf3,mf4,mf5,mf6,mf7,mf8,mf9)	J	W^H parameter of a phase component (see Eq. (6))
aw_Gex_WS (phase_name, model_index, mf1,mf2,mf3,mf4,mf5,mf6,mf7,mf8,mf9)	J/K	W^S parameter of a phase component (see Eq. (6))
aw_Gex_WV (phase_name, model_index, mf1,mf2,mf3,mf4,mf5,mf6,mf7,mf8,mf9)	J/bar	W^V parameter of a phase component (see Eq. (6))

For a mineral equilibrium reaction the thermodynamic relation

$$\Delta G^*_{reaction} = 0 = \sum_i^n v_i \left[\Delta H^0_{f(i)} + \int_{T_0}^{T} C^0_{P(i)}\,\mathrm{d}T + \int_{P_0}^{P} \left(V^0_{(i)} - T\left(\frac{\partial V_{(i)}}{\partial T}\right)_p \right) \mathrm{d}P - T\left(S^0_{(i)} + \int_{T_0}^{T} \frac{C^0_{P(i)}}{T}\,\mathrm{d}T - \int_{P_0}^{P} \left(\frac{\partial V_{(i)}}{\partial T}\right)_p \mathrm{d}P \right)\right] + RT\, ln \prod_i^n a_i^{v_i} \qquad (1)$$

must be satisfied. In this equation $\Delta G^*_{reaction}$ is the Gibbs free energy of a mineral reaction at a given pressure P and temperature T and

v_i	stoichiometric reaction coefficient of phase component i
$\Delta H^0_{f(i)}$	standard state enthalpy of formation of phase component i
$C^0_{P(i)}$	molar heat capacity at constant pressure of phase component i
$V^0_{(i)}$	molar volume at 1 bar and 298.15 K of phase component i
$S^0_{(i)}$	molar entropy at 1 bar and 298.15 K of phase component i
R	gas constant
a_i	activity of phase component i
T_0	reference temperature 298.15 K
P_0	reference pressure 1 bar.

The expression in the square bracket is related to the Gibbs free energy of formation of pure phases at P and T. PTGIBBS uses the empirical equation

$$C^0_P = a + bT + cT^{-2} + dT^{-0.5} + eT^{-1} + fT^{-3} + gT^2 \qquad (2)$$

to describe the temperature dependence of the molar heat capacity C^0_P. For phases that undergo order–disorder transitions or show lambda heat capacity anomalies, further energy terms are added to the free energy function. PTGIBBS can handle this using a tricritical Landau model including pressure dependence (Holland and Powell, 1998) or the additional energy terms $G_{disorder}$ or $G_{transition}$ as formulated by Berman (1988), which can be selected. There are three options available to describe the volume behavior of solid phases. The volume behavior of solid phases as a function of pressure can be expressed, e.g. by the Murnaghan equation of state (EOS). The values for bulk modulus κ and its pressure derivative κ', can be combined with Berman's thermal expansion coefficients (*v1*,*v2*), or with Holland and Powell's (1998) thermal expansion parameter. In the latter case κ' is set to 4. The volume behavior can also be described by the function (of P and T) used by Berman (1988). The thermodynamic data required for computing are read out from an internal data base arranged in a worksheet (see Section 4.1). In addition, a sufficient knowledge of the thermodynamic properties of solid solution phases (i.e. information about the activity of a mineral component in a solid solution phase) is required to calculate the term $RT \ln a_i$ of Eq. (1). Most minerals, however, deviate from ideal behavior. The non-ideality is expressed by the activity coefficient, γ_i, leading to the expression for activity in Eq. (1):

$$a_i = a_i^{ideal} \cdot \gamma_i. \qquad (3)$$

The ideal activity can be expressed in PTGIBBS with

$$a_i^{ideal} = X^{n1}_{site1(i)}\, X^{n2}_{site2(i)} \quad \text{with } n = \text{site multiplicity}. \qquad (4)$$

Diverse formulations for the deviation from the ideal behavior of solid solutions and, thus, for thermodynamic excess quantities are suggested in the literature (e.g., Guggenheim, 1937, 1952; Ganguly and Saxena, 1984). PTGIBBS performs calculations on the basis of the subregular model (Thompson, 1967), which has been extensively used in the recent petrological literature to treat asymmetric solid solutions. The following equation is used for describing the activity coefficient of the *m*th component in a subregular solid solution (Berman, 1990):

$$nRT \ln \gamma_m = \sum_1^p W_{ijk}\left(\frac{Q_m X_i X_j X_k}{X_m} - 2X_i X_j X_k\right), \qquad (5)$$

where n is the site multiplicity, Q_m is an integer that counts the number of i, j, k ($i \leqslant j \leqslant k$, $i \neq k$) that are equal to m, p corresponds to the number of Margules parameters W^G needed for a given system, and X_m is the site fraction of the m*th* component. The P–T dependence of the interaction parameters W_{ijk} is expressed by

$$W_{ijk} = W^H_{ijk} - TW^S_{ijk} + PW^V_{ijk}. \qquad (6)$$

W^U_{ijk} instead of W^H_{ijk} is used by Chatterjee (1991). Eq. (5) also enables the application of a regular model, which is restricted to symmetrical solid solutions. The interaction parameter of a regular solution is a function of the energetic interaction between atoms in a crystal structure and can be interpreted on a firm physical foundation. The activity coefficients of the phase components in an n component system can be expressed by

$$RT \ln \gamma_k = \sum_{i \neq k} X_i(1 - X_k)w_{ik} - \sum_{i \neq k}\sum_{j \neq k} X_i X_j w_{ij}, \qquad (i \neq j). \qquad (7)$$

The reduction of the asymmetric expression of Eq. (5) to the symmetric form can be achieved by equating all binary Margules parameters ($W_{iij} = W_{ijj}$) in the sub-systems and the use of all possible ternary parameters W_{ijk} with

$$W_{ijk} = (W_{iij} + W_{ijj} + W_{iik} + W_{ikk} + W_{jjk} + W_{jkk})/2 \tag{8}$$

PTGIBBS solves the nonlinear Eq. (1) for P and T by iterative techniques in order to locate several points of the equilibrium curve in the P–T space. If water fluid participates in the reaction, the volume–pressure integrals of Eq. (1) for H_2O are replaced by the energy term $RT \ln f_{H_2O}$. An external routine based on the equations introduced by Holland and Powell (1998) computes this energy term. At present, no reactions with CO_2 and CO can be calculated.

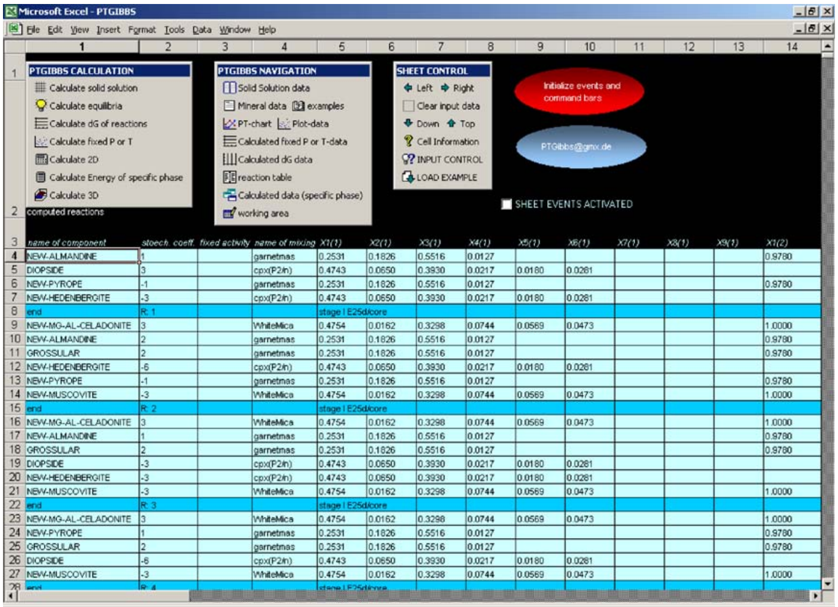
4. Program description

PTGIBBS consists of 15 worksheets. Each sheet is equipped with its own command bar to navigate within the entire program and run different calculation procedures. After starting PTGIBBS the worksheet "Input" is automatically activated (Fig. 1). In this worksheet mineral equilibria can be entered for computation. The thermodynamic data of pure mineral phases, the definition of components of solid solution phases and the thermodynamic parameters for the corresponding solid solutions are located in the worksheets "mineral_data", "mixmod" and "mixparam" , respectively. For users who want to develop their own worksheet applications using the available thermodynamic functions built into PTGIBBS (see Table 1) a blank worksheet named "working_area" is provided.

The remaining 10 sheets primarily present the results by tables or charts. They are also automatically activated after respective computation procedures. Table 2 concisely describes all worksheets. In the following, the major worksheets are explained in more detail.

4.1. Worksheet "mineral_data"

The worksheet "mineral_data" contains the internally consistent thermodynamic data of pure mineral phases by Holland and Powell (1998) and by Berman (1988). In addition, mineral data compatible with the internally consistent data set of Berman (1988), published by Berman (1990), Brandelik and Massonne (2001), Evans (1990), Lattard and Evans (1992), Lattard and Le Breton (1994), Massonne (1991, 1992a, 1995a–c), Massonne and Szpurka (1997), Massonne et al. (1993, 2003), Rosenbleck (1996) and Stöckhert et al. (1997), are enclosed. In the present version, data for 266 phases (some by more than 1 data set) are arranged in a table of the worksheet. Comments in the sheet provide information on the thermodynamic parameters in the database



	1	2	3	4	5	6	7	8	9	10	11	12	13	14
3	name of component	stoech. coeff.	fixed activity	name of mixing	X1(1)	X2(1)	X3(1)	X4(1)	X5(1)	X6(1)	X7(1)	X8(1)	X9(1)	X1(2)
4	NEW-ALMANDINE	1		garnetmas	0.2531	0.1826	0.5516	0.0127						0.9780
5	DIOPSIDE	3		cpx(P2/n)	0.4743	0.0650	0.3930	0.0217	0.0180	0.0281				
6	NEW-PYROPE	-1		garnetmas	0.2531	0.1826	0.5516	0.0127						0.9780
7	NEW-HEDENBERGITE	-3		cpx(P2/n)	0.4743	0.0650	0.3930	0.0217	0.0180	0.0281				
8	end	R: 1			stage I E25d/core									
9	NEW-MG-AL-CELADONITE	3		WhiteMica	0.4754	0.0162	0.3298	0.0744	0.0569	0.0473				1.0000
10	NEW-ALMANDINE	2		garnetmas	0.2531	0.1826	0.5516	0.0127						0.9780
11	GROSSULAR	2		garnetmas	0.2531	0.1826	0.5516	0.0127						0.9780
12	NEW-HEDENBERGITE	-6		cpx(P2/n)	0.4743	0.0650	0.3930	0.0217	0.0180	0.0281				
13	NEW-PYROPE	-1		garnetmas	0.2531	0.1826	0.5516	0.0127						0.9780
14	NEW-MUSCOVITE	-3		WhiteMica	0.4754	0.0162	0.3298	0.0744	0.0569	0.0473				1.0000
15	end	R: 2			stage I E25d/core									
16	NEW-MG-AL-CELADONITE	3		WhiteMica	0.4754	0.0162	0.3298	0.0744	0.0569	0.0473				1.0000
17	NEW-ALMANDINE	1		garnetmas	0.2531	0.1826	0.5516	0.0127						0.9780
18	GROSSULAR	2		garnetmas	0.2531	0.1826	0.5516	0.0127						0.9780
19	DIOPSIDE	-3		cpx(P2/n)	0.4743	0.0650	0.3930	0.0217	0.0180	0.0281				
20	NEW-HEDENBERGITE	-3		cpx(P2/n)	0.4743	0.0650	0.3930	0.0217	0.0180	0.0281				
21	NEW-MUSCOVITE	-3		WhiteMica	0.4754	0.0162	0.3298	0.0744	0.0569	0.0473				1.0000
22	end	R: 3			stage I E25d/core									
23	NEW-MG-AL-CELADONITE	3		WhiteMica	0.4754	0.0162	0.3298	0.0744	0.0569	0.0473				1.0000
24	NEW-PYROPE	1		garnetmas	0.2531	0.1826	0.5516	0.0127						0.9780
25	GROSSULAR	2		garnetmas	0.2531	0.1826	0.5516	0.0127						0.9780
26	DIOPSIDE	-6		cpx(P2/n)	0.4743	0.0650	0.3930	0.0217	0.0180	0.0281				
27	NEW-MUSCOVITE	-3		WhiteMica	0.4754	0.0162	0.3298	0.0744	0.0569	0.0473				1.0000
28	end	R: 4			stage I E25d/core									

Fig. 1. Screenshot of worksheet "Input" after loading working example 4. Mineral equilibria to be computed and compositional information on solid solutions, are arranged in cells of this sheet. Control buttons in three command bars above input grid allow a simple navigation in the workbook and start of different computation routines.

Table 2
Short description of worksheets included in PTGIBBS

Name of worksheet	Short Description
Input	is the main worksheet, in which mineral equilibria are entered for computation. It is automatically activated after starting PTGIBBS. Start of computation routines and navigation in workbook can be achieved from here.
mineral_data	thermodynamic data of minerals are arranged in this sheet.
mixmod	comprises defined mixing models.
mixparam	contains corresponding mixing parameters of models defined in worksheet "mixmod".
PT-PLOT	displays calculated equilibria curves in a *PT*-chart.
PT_data	presents computed *P* and *T* data of equilibria calculations.
result_CfixedPT	shows result of computation routine "Calculate fixed *PT*" by a table and charts.
result_CdG	displays result of computation routine "Calculate d*G* of reactions" in a table and by a chart.
result_Cspecificphase	presents result of computation routine "Calculate data for specific phase".
working _area	An empty worksheet for users who want to develop pure spreadsheet applications based on available thermodynamic functions built in PTGIBBS.
reaction_list	lists calculated reactions.
reactions	is an internal worksheet of PTGIBBS used for calculation.
examples	contains examples. Further examples can be added.
2D_PLOT	presents result of computation routine "Calculate 2D".
3D_PLOT	displays result of computation routine "Calculate 3D".

and additional references. Table 3 shows the type and position of thermodynamic input data in the worksheet. Phases related to the data set by Holland and Powell (1998) are written in small case letters. Those belonging to the data set of Berman (1988) are presented in capitals. The remaining phases compatible with Berman's (1988) data set have the name prefix 'NEW' and are also written in capitals. Additional phases can be inserted arbitrarily, but it is important to note that no empty rows are allowed between phase entries and that no columns can be inserted.

4.2. Worksheet "mixmod"

In the worksheet "mixmod", the mixing models of solid solution phases (see Table 4) are arranged in columns. Additional models can be defined and added to the worksheet (maximum 255). They must be entered in the next free column. The principal structure is shown in Table 5. The sheet contains the name of the models, the name of the components, multiplicities of structural sites, and the number of lines for Margules parameters (see worksheet "mixparam") used in the corresponding model. The component names written in the worksheet "Input" must exactly match those in the thermodynamic data set including small case and capital letters. PTGIBBS can compute extended mixing models with a maximum of nine components for each solid solution phase. Non-ideal behavior can be modelled for only one structural site. However, for a second structural site a site multiplicity can be defined. The Margules parameters of a specific solid solution model can be viewed by clicking on the button "SHOW MIXING PARAMETERS" and selecting the specific model.

4.3. Worksheet "mixparam"

The mixing parameters for the computation of the deviation of a specific solid solution from its ideal mixing behavior on the basis of Eq. (5) are located in the worksheet "mixparam" in a table. Table 6 shows the structure of the data input for the model "garnetmas". In the columns 3 (C), 4 (D), and 5 (E) of the worksheet, numbers for the subscripts (see Eq. (5)) of the interaction parameters are given. The corresponding excess enthalpy parameters (W^H), excess entropy parameters (W^S) and excess volume parameters (W^V) are arranged in columns 6 (F), 7 (G), and 8 (H), respectively. There is no preference in the sequence of the subscripts of columns 3 (C)–5 (E), but no empty rows are admitted. It is also impossible to insert new rows in this worksheet. The possibility of using a maximum of 468 mixing parameters for one solid solution model allows the computation of extensive solid solution models. A control procedure to check for correct input is started after the deactivation of the worksheet and provides information about possible type error.

4.4. Worksheet "Input"

After the activation of the worksheet "Input", three command bars appear in the upper portion of the screen as separate windows (Fig. 1). They allow simple navigation in the workbook and the start of different

Table 3
Description of data structure in worksheet "mineral_data". Reference conditions: $T_r = 298.15\,\mathrm{K}$ and $P_r = 1\,\mathrm{bar}$. PTGIBBS supports three different ways to describe volume behavior of solids (volume segments 1–3). If one segment is used, cell entries in two other segments must be empty

Column	Entry	Molar units	Description	Segment
1	Name of Phase			
3	$\Delta_f H^{(Tr,Pr)}$	J	Enthalpy of formation from elements at T_r and P_r	Standard state
4	$\sigma(\Delta_f H^{(Tr,Pr)})$	J	Standard deviation of enthalpy of formation (see Holland and Powell 1998)	
5	$S^{(Tr,Pr)}$	$\mathrm{J\,K^{-1}}$	Third law entropy at T_r and P_r	
6	$V^{(Tr,Pr)}$	$\mathrm{J\,bar^{-1}}$	Molar volume at T_r and P_r	
7	a	$\mathrm{J\,K^{-1}}$	Heat capacity coefficients according to	Heat capacity
8	b	$\mathrm{J\,K^{-2}}$		
9	c	J K	$Cp(T) = a + bT + cT^{-2} + dT^{-0.5} + eT^{-1} + fT^{-3} + gT^2$	
10	d	$\mathrm{J\,K^{-0.5}}$	a = Berman's (1988) k_0	
11	e	J	c = Berman's (1988) k_2	
12	f	$\mathrm{J\,K^{2}}$	d = Berman's (1988) k_1	
13	g	$\mathrm{J\,K^{-3}}$	f = Berman's (1988) k_3	
14	a^0	$\mathrm{K^{-1}}$	Thermal expansion parameter and	Volume 1
15	κ	bar	bulk modulus at 298.15 K according to Murnaghan-EOS-data used by Holland and Powell (1998)	
16	T_c	K	Landau parameter according to Holland and Powell (1998)	Landau
17	S_{max}	$\mathrm{J\,K^{-1}}$	Landau parameter according to Holland and Powell (1998)	
18	V_{max}	$\mathrm{J\,bar^{-1}}$	Landau parameter according to Holland and Powell (1998)	
19	$v1$	$\mathrm{K^{-1}}$	Parameters for thermal expansivity	Volume 2
20	$v2$	$\mathrm{K^{-2}}$	$V(T, 1\,\mathrm{bar}) = V0(1 + v1(T - T_\mathrm{r}) + v2(T - T_\mathrm{r})^2)$	(Murnaghan EOS)
21	κ	bar	Bulk modulus at 298.15 K	
22	κ'		First pressure-derivative of bulk modulus	
23	$v1$	$\mathrm{K^{-1}}$	Parameters for thermal expansivity and compressibility	Volume 3
24	$v2$	$\mathrm{K^{-2}}$	$V(P,T) = V0[1 + v1(T - T_\mathrm{r}) + v2(T - T_\mathrm{r})^2 + v3(P - P_\mathrm{r}) + v4(P - P_\mathrm{r})^2]$	(as in Ge0-Calc)
25	$v3$	$\mathrm{bar^{-1}}$		
26	$v4$	$\mathrm{bar^{-2}}$		
27	$d0$	$\mathrm{J\,K^{-1}}$	Disorder equation according to Berman (1988)	Disorder data
28	$d1$	$\mathrm{J\,K^{-0.5}}$		(as in Ge0-Calc)
29	$d2$	J K		
30	$d3$	$\mathrm{J\,K^{2}}$	$Cp_\mathrm{dis} = d0 + d1\,T^{-0.5} + d2\,T^{-2} + d3\,T^{-3}$	
31	$d4$	J	$+ d4\,T^{-1} + d5\,T + d6\,T^2$	
32	$d5$	$\mathrm{J\,K^{-2}}$		
33	$d6$	$\mathrm{J\,K^{-3}}$		
34	T_{min}	K	Reference temperature (onset of disordering)	
35	T_{max}	K	Reference temperature (at higher temperatures phase is fully disordered).	
36	dv		This parameter scales enthalpy to volume of disorder corresponding to Berman's d_5 parameter (Berman, 1988)	
37	$T1$	K	Transition temperature	Transition data (as in Ge0-Calc, but only one transition is supported)
38	$T2$	K	Reference temperature setting a lower integration limit	
39	$T3$	$\mathrm{J^{0.5}K^{-1}}$	λ–Cp term L_1 $\mathrm{Cp}(\lambda) = \mathrm{T}(\mathrm{L}_1 + \mathrm{L}_2\mathrm{T})^2$ (see Berman and Brown , 1985)	
40	$T4$	$\mathrm{J^{0.5}\,K^{-2}}$	λ–Cp term L_2 $\mathrm{Cp}(\lambda) = \mathrm{T}(\mathrm{L}_1 + \mathrm{L}_2\mathrm{T})^2$ (see Berman and Brown , 1985)	
41	$T5$	J	First-order portion of enthalpy of transition	
42	$T6$	$\mathrm{K\,bar^{-1}}$	dT/dP slope of transition	
47	Formula			

Table 4
Sources of mixing models included in worksheet "mixmod"

Name of mixing model	Phase	Source
Ti_garnet	Garnet	Unpublished, revised form of Brandelik and Massonne (2001)
WhiteMica	Mica	Massonne and Szpurka (1997)
Ti-muscovite	Mica	Massonne et al. (1993)
cpx(C2/c)	C2/c-clinopyroxene	Massonne (1995a)
cpx(P2/n)	P2/n-clinopyroxene	Massonne (1995a)
PLAG	Plagioclase	Fuhrman and Lindsley (1988)
AMPH	Amphibole	Massonne (1992b)
garnetmas	Garnet	Massonne (1995a)
garnetberman	Garnet	Berman (1990)
garnetGS	Garnet	Ganguly and Saxena (1984)
Olivine	Olivine	Massonne (1995a)
OPX	Orthopyroxene	Unpublished extension of model in Massonne (1995a)
Ti_garnet2001	Garnet	Brandelik and Massonne (2001)

Table 5
Example for input structure of mixing model "garnetmas" defined in worksheet "mixmod" (see Table 4)

Name of mixing model	Garnetmas
Name of component 1	GROSSULAR
Name of component 2	NEW-PYROPE
Name of component 3	NEW-ALMANDINE
Name of component 4	SPESSARTINE
Name of component 5	
Name of component 6	
Name of component 7	
Name of component 8	
Name of component 9	
Site multiplicity (structural site 1)	3
Number of lines in model	14
Name of component (structural site 2)	xAl
Site multiplicity (structural site 2)	2

computation routines. The input of equilibria for computation begins in row 4. Names of phases participating in the equilibria and the related stoichiometric coefficients are provided in columns 1 (A) and 2 (B), respectively. Negative numbers for the stoichiometric coefficients mean that the corresponding phase takes part on the high temperature side of the equilibrium. For equilibrium computations including solid solutions, the name of the mixing model has to be inserted in column 4 (D). In the cells of columns 5 (E)–14 (N) site fractions or mole fractions (depending on the solid solution model defined in the worksheet "mixmod") can be entered. The number of site/mole fractions and their positions in the worksheet must exactly correspond to the solid solution model (see worksheet "mixmod") used. Alternatively, fixed activities can be entered in column 3 (C). In this case, the numbers in the cells of columns 5 (E)–14 (N) are ignored in the computations. Each equilibrium must be finished with the entry "end" in column 1 (A). In this row, a comment can be added in column 5 (E). For deltaG computations of equilibria at defined P–T conditions and fixed P–T calculations, additional data for temperature (in °C) in column 3 (C) and pressure (in bar) in column 4 (D) must be added in the "end" rows. A number of control procedures are automatically started before running a computation routine. These procedures try to minimize input errors and report these errors until correct input is given. By clicking on the button "LOAD EXAMPLE" input examples (see Section 5) can be initialized in order to view the input structure. In order to view the nature of the data in a cell, click on that cell and then on "Cell information" in the "SHEET CONTROL" command bar.

During manual input the user should activate the check box "SHEET EVENTS ACTIVATED" on the upper right above the worksheet. Doing this enables event-driven procedures to automatically format the table of the "Input" worksheet and calculate formulas from data entered by the user. The computation routines available in PTGIBBS are run by clicking on the control buttons arranged in the command bar "PTGIBBS CALCULATION". In the following, the control buttons are described.

4.5. *Computation routines*

4.5.1. *"Calculate equilibria"*

After starting the routine "Calculate equilibria" a dialogue is displayed, in which a selection of the equilibria, provided in the worksheet "Input", can be

Table 6
Example for input structure of mixing parameters, which is related to model “garnetmas” defined in worksheet “mixparam”

			Garnetmas	Name of mixing model	
			GROSSULAR	Name of component 1	
			NEW-PYROPE	Name of component 2	
			NEW-ALMANDINE	Name of component 3	
			SPESSARTINE	Name of component 4	
				Name of component 5	
				Name of component 6	
				Name of component 7	
				Name of component 8	
				Name of component 9	
			3	Site multiplicity (structural site)	
			W^H	W^S	W^V
1	1	2	21560	−31.718	0.1
1	2	2	69200	29.829	0.1
1	1	3	20320	5.08	0.17
1	3	3	2620	5.08	0.09
2	2	3	230	0	0.01
2	3	3	3720	0	0.06
2	2	4	13500	0	0
2	4	4	13500	0	0
3	3	4	1757	0	0
3	4	4	1757	0	0
1	2	3	58825	4.136	0.265
1	2	4	58880	−0.945	0.1
1	3	4	13227	5.08	0.13
2	3	4	17232	0	0.035

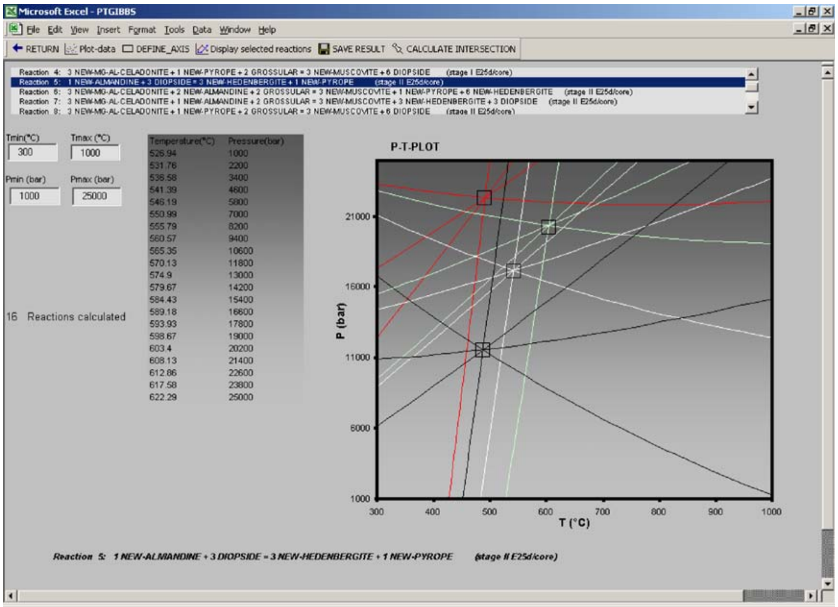
undertaken for further computations. The subsequent dialogue requests a definition of the *P–T* range for the computation. At the end of the calculation the software directly displays the resulting *P–T* plot by opening the worksheet “PT_PLOT” (Fig. 2). By clicking on a specific equilibrium curve in the *P–T* plot, the *P–T* data and the equation of the corresponding reaction (with comments) are simultaneously displayed. An ActiveX list box is located at the top of the worksheet “PT_PLOT” listing the equations of the calculated reactions. By selecting a reaction there, the corresponding curve is automatically assigned in the chart. Additional procedures can be run by clicking on one of several control buttons arranged in the command bar. By means of an interactively operating system it is possible, e.g. to calculate the intersection between two curves, to display only selected curves, or to save the results of the calculation in a new workbook. The latter also refers to the *P–T* plot itself by using the “copy” function of EXCEL™.

4.5.2. *“Calculate for fixed P or T”*

For the calculation of equilibrium temperatures at given pressures or vice versa the subroutine “Calculate for fixed *P* or *T*” can be used. It is necessary to enter values for *P* and/or *T* as explained in Section 4.4 (see example 5). For a specific geothermobarometer, up to a thousand different mineral compositions can be considered in one calculation step. This requires, however, the input of the corresponding equilibrium as often as up to a thousand times. A program which facilitates the input work including the transmission of analytical data (site/mole fractions) obtained at an electron microprobe is currently under work (Brandelik, in preparation). The procedure “Calculate for fixed *P* or *T*” should therefore be useful for the application of geothermobarometers. The result is automatically presented in the worksheet “result_CfixedPT” including two charts.

4.5.3. *“Calculate dG of reactions”*

The computation of the Gibbs free energy at fixed *P–T* conditions (same input as 4.5.2) for a selected equilibrium can be achieved with the routine “Calculate dG of reactions”. This procedure was designed for the calibration of new geothermobarometers from natural mineral assemblages and experimental data. For instance, the energy resulting from a non-ideal mixing behavior can be computed for a large number of *P*, *T*,



Reaction 4: 3 NEW-MG-AL-CELADONITE + 1 NEW-PYROPE + 2 GROSSULAR = 3 NEW-MUSCOVITE + 6 DIOPSIDE (stage I E25d/core)
Reaction 5: 1 NEW-ALMANDINE + 3 DIOPSIDE = 3 NEW-HEDENBERGITE + 1 NEW-PYROPE (stage II E25d/core)
Reaction 6: 3 NEW-MG-AL-CELADONITE + 2 NEW-ALMANDINE + 2 GROSSULAR = 3 NEW-MUSCOVITE + 1 NEW-PYROPE + 6 NEW-HEDENBERGITE (stage II E25d/core)
Reaction 7: 3 NEW-MG-AL-CELADONITE + 1 NEW-ALMANDINE + 2 GROSSULAR = 3 NEW-MUSCOVITE + 3 NEW-HEDENBERGITE + 3 DIOPSIDE (stage II E25d/core)
Reaction 8: 3 NEW-MG-AL-CELADONITE + 1 NEW-PYROPE + 2 GROSSULAR = 3 NEW-MUSCOVITE + 6 DIOPSIDE (stage II E25d/core)

Tmin(°C): 300
Tmax (°C): 1000
Pmin (bar): 1000
Pmax (bar): 25000

16 Reactions calculated

Temperature(°C)	Pressure(bar)
526.94	1000
531.76	2200
536.58	3400
541.39	4600
546.19	5800
550.99	7000
555.79	8200
560.57	9400
565.35	10600
570.13	11800
574.9	13000
579.67	14200
584.43	15400
589.18	16600
593.93	17800
598.67	19000
603.4	20200
608.13	21400
612.86	22600
617.58	23800
622.29	25000

Reaction 5: 1 NEW-ALMANDINE + 3 DIOPSIDE = 3 NEW-HEDENBERGITE + 1 NEW-PYROPE (stage II E25d/core)

Fig. 2. Screenshot of worksheet "PT_PLOT" after calculation of working example 4. This worksheet is automatically activated after computation using "Calculate equilibria". Four squares in P–T diagram, showing location of invariant points, were introduced after opening this worksheet using drawing tools of EXCEL$^{\text{TM}}$.

and X data. After the calculation, the results are automatically listed in the worksheet "result_CdG". A chart visualizes the computation results.

4.5.4. *"Calculate solid solution"*

The routine "Calculate solid solution" allows the simultaneous computation of several energy parameters for a large number of compositions of a particular mineral entered in the worksheet "Input". The program also accepts a somewhat modified input structure compared to that shown in Fig. 1. For each entry the name of the phase for which energy parameters are being calculated is entered in column 1 (A). These would be followed by compositional data entered into columns 5 (E)–14 (N) as described for the Input table (Fig. 1). The last entry in column 1 (A) must be "end". Using formulas and the reproduction function of EXCEL$^{\text{TM}}$, a large number of different mineral compositions can easily be produced (columns 5 (E)–14 (N)). Several different energy terms and other parameters of a component in a solid solution can be computed, e.g. the ideal and real activity, the activity coefficient γ, the total Gibbs energy of mixing G^{mix}, the excess Gibbs energy of mixing G^{Ex}, and the parameters W^H, W^S, and W^V. In columns 50 (AX) and 51 (AY), data for temperature (°C) and pressure (bar) can be typed in, when necessary, before starting the procedure. The results of the calculation are presented in columns 41 (AO)–49 (AW) and 52 (AZ)–53 (BA) of the worksheet "Input". They allow the creation of various diagrams such as the a-X-diagram of Fig. 3.

4.5.5. *"Calculate data for specific phase"*

Various energy parameters for a selected phase at given P and T (Fig. 4) can be calculated with the internal program "Calculate data for specific phase". In contrast to the previous routines, this program does not require entries on the "Input" sheet. The program is completely driven by dialogues and events. After selecting the phase from a list box, the code checks for possible solid solution models. If solid solution models are available, they can be selected from an additional list box created automatically (see Fig. 4). The input boxes for site (or mole) fractions within the window are automatically displayed depending on the solid solution model. The computation is started by clicking on the button "Calculate". The results are presented in the same window on the right-hand side. The input can be changed and the calculations can be repeated. By activating the "send mode", results of each computation are written into the worksheet "result_Cspecificphase". After finishing the program, the worksheet can also be displayed by means of the button "Calculated data (specific phase)" in the command bar "PTGIBBS NAVIGATION".

4.5.6. *"Calculate 2D" and "Calculate 3D"*

The routines "Calculate 2D" and "Calculate 3D" enable the display of diverse thermodynamic data of a selected phase as a function of *P* or *T* and *P* and *T*, respectively, in a chart. Again, no input within the range of the worksheet "Input" is necessary (Fig. 5). As for the previous program (Section 4.5.5), an entirely event-driven input in the form of a dialogue is started after selecting a phase and a function. Afterwards, the results will appear by clicking on the button "Create 2D plot" or "Create 3D plot" (Fig. 6). In the latter case the spacial orientation of the chart can easily be changed by means of the scroll bars. By clicking on the button "Copy 2D data" or "Copy 3D data", the computed data are copied to the clipboard.

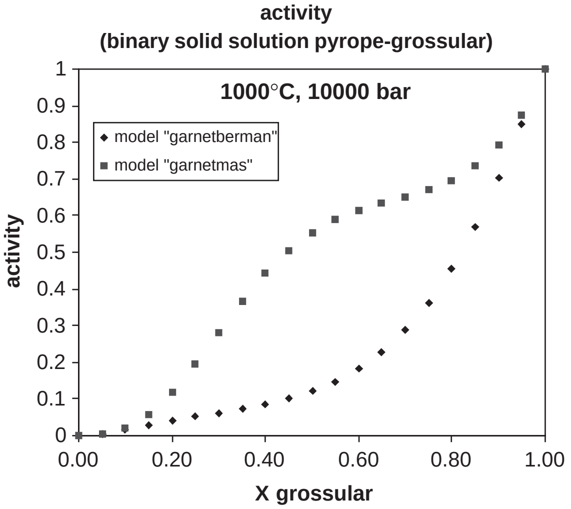


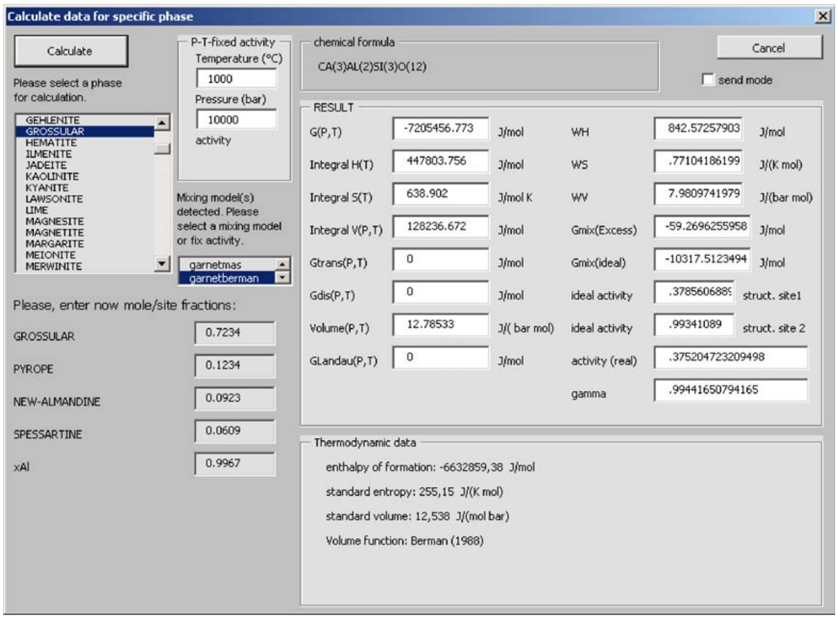
Fig. 3. a-X-diagram showing activities of grossular component for binary solid solution series pyrope-grossular, obtained with "Calculate solid solution" for 1000°C and 10000 bar for two different garnet solid solution models (working example 6).

5. Working examples

To demonstrate the versatility of PTGIBBS, several working examples are presented. The corresponding data can be loaded into the "Input" sheet by clicking on the button "LOAD EXAMPLE" in the "SHEET CONTROL" window. A dialogue opens from which the examples 1–6 can be selected.

5.1. *Example 1*

Our first example is related to the *P*–*T* position of the coesite–quartz transition curve. After loading this example, the transition curves can be simultaneously calculated with different thermodynamic data. In the example, the data set by Holland and Powell (1998) and by Berman (1988) is used. A third *P*–*T* curve is calculated with modified coesite data (NEW-COESITE;



Please select a phase for calculation.

P-T-fixed activity
Temperature (°C) 1000
Pressure (bar) 10000
activity

Mixing model(s) detected. Please select a mixing model or fix activity.

chemical formula
CA(3)AL(2)SI(3)O(12)

☐ send mode

Please, enter now mole/site fractions:

GROSSULAR 0.7234
PYROPE 0.1234
NEW-ALMANDINE 0.0923
SPESSARTINE 0.0609
xAl 0.9967

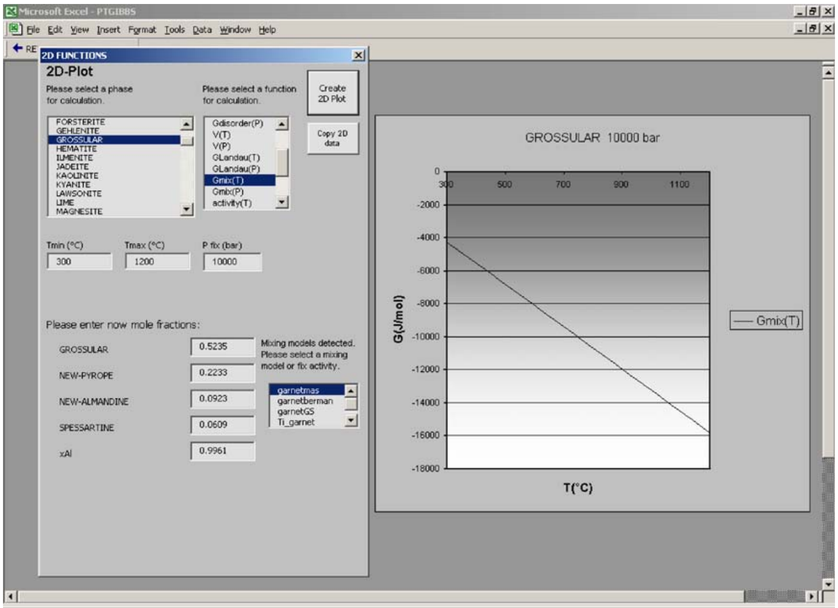
RESULT

G(P,T)	-7205456.773	J/mol	WH	842.57257903	J/mol
Integral H(T)	447803.756	J/mol	WS	.77104186199	J/(K mol)
Integral S(T)	638.902	J/mol K	WV	7.9809741979	J/(bar mol)
Integral V(P,T)	128236.672	J/mol	Gmix(Excess)	-59.2696255958	J/mol
Gtrans(P,T)	0	J/mol	Gmix(ideal)	-10317.5123494	J/mol
Gdis(P,T)	0	J/mol	ideal activity	.378560688	struct. site1
Volume(P,T)	12.78533	J/(bar mol)	ideal activity	.99341089	struct. site 2
GLandau(P,T)	0	J/mol	activity (real)	.375204723209498	
			gamma	.99441650794165	

Thermodynamic data

enthalpy of formation: -6632859,38 J/mol
standard entropy: 255,15 J/(K mol)
standard volume: 12,538 J/(mol bar)
Volume function: Berman (1988)

Fig. 4. Screenshot of dialogue related to sub-routine "Calculate data for specific phase" to calculate various data of a specific phase at a given temperature and pressure. Computation was done for garnet component grossular, activity formulation by Berman (1990), and an arbitrarily selected garnet composition.



Tmin (°C) 300

Tmax (°C) 1200

P fix (bar) 10000

Please enter now mole fractions:

GROSSULAR 0.5235

NEW-PYROPE 0.2233

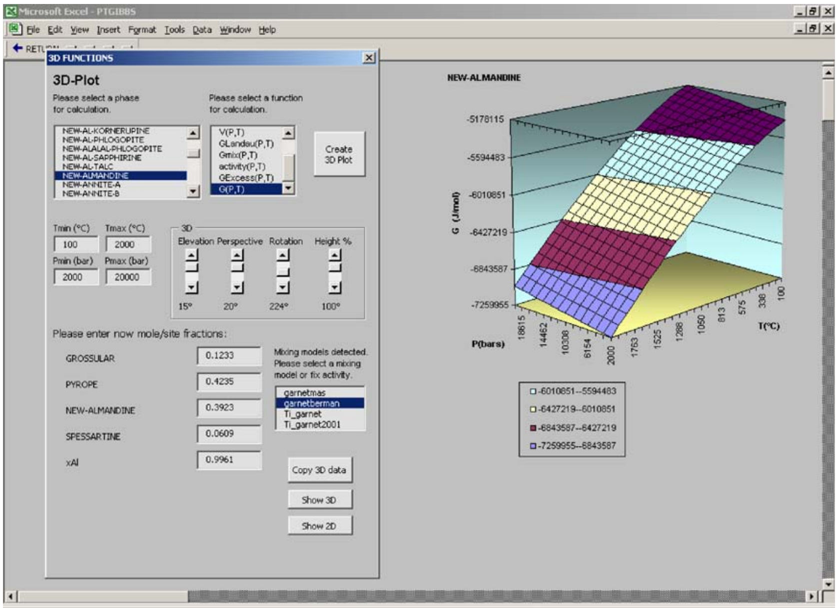
NEW-ALMANDINE 0.0923

SPESSARTINE 0.0609

xAl 0.9961

Mixing models detected. Please select a mixing model or fix activity.

Fig. 5. Screenshot after calculating thermodynamic function "Gmix(T)" for grossular using activity formulation for garnet components ("garnetmas") of Massonne (1995a). Input and list boxes within window "2D FUNCTIONS" are automatically displayed depending on selected function.



Tmin (°C) 100

Tmax (°C) 2000

Pmin (bar) 2000

Pmax (bar) 20000

3D

Elevation	Perspective	Rotation	Height %
15°	20°	224°	100°

Please enter now mole/site fractions:

GROSSULAR 0.1233

PYROPE 0.4235

NEW-ALMANDINE 0.3923

SPESSARTINE 0.0609

xAl 0.9961

Mixing models detected. Please select a mixing model or fix activity.

Fig. 6. Screenshot after calculating a 3D-diagram of free Gibbs energy $G\ (P,T)$ of almandine component in garnet. Computation was done for garnet solid solution model "garnetberman" (Berman, 1990) and an arbitrarily selected garnet composition.

Massonne, 1992b) which are compatible with the data set by Berman. With these data, the experimentally determined coesite–quartz transition curve by Mirwald and Massonne (1980) can be perfectly reproduced.

5.2. Examples 2 and 3

Two further examples are related to reaction curves with pure mineral phases. Example 2 concerns the breakdown reaction of pyrophyllite yielding quartz, kyanite, and H_2O. In this example, data from the data set by Holland and Powell (1998) are used. Two different reaction curves are calculated simultaneously by setting the water activity to 0.8 in the first reaction (lines 4–8) and 0.9 in the second reaction (lines 9–13).

Example 3 is related to the three univariant equilibrium curves in the system Al_2SiO_5 and the stability fields of andalusite, kyanite, and sillimanite. Thermodynamic data by Berman (1988) are used for the calculation. As in the above examples, the worksheet "PT_PLOT" appears showing the reaction curves. After using the button "Calculate intersection" and selecting two reactions (see 4.5.1), the *P*–*T* position of the triple point can be calculated to give 3732.82 bar and 505.56 °C.

5.3. Examples 4 and 5

Example 4 is related to an eclogite from the Saxonian Erzgebirge (Massonne, 1992a). Equilibria involving muscovite and Mg–Al-celadonite components in phengite, diopside and hedenbergite components in omphacite, and grossular, pyrope and almandine components in garnet define a single *P*–*T*-point. PTGIBBS allows the computation of this point by determining the *P*–*T* positions of the equilibria

(1) $Fe_3Al_2Si_3O_{12} + 3\,CaMgSi_2O_6 = Mg_3Al_2Si_3O_{12} + 3\,CaFeSi_2O_6$,
(2) $3\,KMgAlSi_4O_{12}(OH)_2 + 2\,Fe_3Al_2Si_3O_{12} + 2\,Ca_3Al_2Si_3O_{12} = 6\,CaFeSi_2O_6 + Mg_3Al_2Si_3O_{12} + 3\,KAl_3Si_3O_{10}(OH)_2$,
(3) $3\,KMgAlSi_4O_{12}(OH)_2 + Fe_3Al_2Si_3O_{12} + 2\,Ca_3Al_2Si_3O_{12} = 3\,CaMgSi_2O_6 + 3\,CaFeSi_2O_6 + 3\,KAl_3Si_3O_{10}(OH)_2$,
(4) $3\,KMgAlSi_4O_{12}(OH)_2 + Mg_3Al_2Si_3O_{12} + 2\,Ca_3Al_2Si_3O_{12} = 6\,CaMgSi_2O_6 + 3\,KAl_3Si_3O_{10}(OH)_2$,

and by subsequently using the "Calculate intersection" function. Several *P*–*T* points and, thus, a *P*–*T*-path, can be calculated for selected phengite, omphacite and garnet compositions, assumed to be in equilibrium at a specific metamorphic stage, from chemically zoned minerals in the corresponding rock. Massonne (1992a) defined four stages by four chemically different mineral triplets (garnet, omphacite, phengite). By clicking on the command button "LOAD EXAMPLE" and selecting "Example 4" in the opening dialogue the input shows these selected compositions (Fig. 1) in terms of mole fractions (see corresponding solid solution model). After starting the routine "Calculate equilibria" the button "SELECT ALL" has to be clicked in the opening dialogue. In the next dialogue, the *P*–*T* range for the computation must be defined (e.g., 1000–25000 bar, 300–1000 °C). After calculation, the result is displayed in the worksheet "PT_PLOT" (Fig. 2). The *P*–*T* data for the four invariant *P*–*T*-points of the four stages were calculated by means of the interactive program "CALCULATE INTERSECTION", and are presented in Table 7. The results are almost identical to those given by Massonne (1992a), although the white mica solid solution model was somewhat modified by Massonne and Szpurka (1997) compared to the previously used model. However, all other thermodynamic data for the above equilibria remained unchanged.

Example 5 addresses a problem similar to the previous example. Again an eclogite is considered. It is from the Franciscan formation (Junction school eclogite near Healdsburg), California. Massonne (1995a) determined ultrahigh pressure conditions for an early metamorphic stage of this eclogite. We used the corresponding compositional relations given by Massonne (1995a) and thermodynamic data as for example 4. In addition to the original work, equilibria are also considered using the phengite component Fe–Al-celadonite (NEW-FE-AL-CELADONITE-B). Altogether, 11 equilibria can be defined (not all are independent from each other) and downloaded as example 5. After calculating the *P*–*T* positions of the corresponding curves (e.g. for the range 1000–40000 bar and 300–700 °C) several intersections appear. Theoretically, these intersections fall in one *P*–*T* point but due to imperfections in the thermodynamic and compositional data, this is not the case. Nevertheless, the results of this example are compatible with *P*–*T* conditions close to 30.6 kbar and 518 °C for the early metamorphic stage of the selected eclogite previously determined by Massonne (1995a).

5.4. Example 6

The last example is related to the calculation of an activity-composition (a-*X*)-diagram for the binary solid solution series pyrope-grossular. After loading example 6, garnet compositions are displayed varying in steps of *X* = 0.05. First, these compositions are assigned to the garnet solid solution model "garnetmas" (Massonne, 1995a). Below, the same compositions appear again but related to the model by Berman (1990). After starting the routine "Calculate solid solution" several different energy terms and other parameters of the garnet components are computed and presented in the columns 41 (AO)–49 (AW) and 52 (AZ)–53 (BA)

Table 7
Calculated temperatures and pressures for four stages of working example 4

	Calc. *T* (°C)	Calc. *P* (bar)
Stage I	491	22332
Stage II	604	20355
Stage IIIa	541	17167
Stage IIIb	487	11561

of the worksheet "Input" (see Chapter 4.5.4). By means of EXCEL™, a chart can easily be inserted and connected with the calculated data in column 48 (AV) and compositional data in column 5 (E). The corresponding graph is shown in Fig. 3.

6. System requirements and availability of the program

PTGIBBS requires complete Microsoft® EXCEL™ installation (version 8.0 or version 9.0) on an IBM-compatible personal computer. The minimum system requirements are a Pentium III 1000 MHZ processor (or equivalent) and 128 RAM memory. For a good performance a minimum screen resolution of 1024 × 768 is recommended. Before running PTGIBBS it is suggested to read the README file included in the PTGIBBS package as, for instance, the EXCEL™ Solver add-in could cause problems. The PTGIBBS package is available from the authors.

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