

## Introduction

The first 4 volumes of this series, under the general heading Thermodynamic Properties of Inorganic Materials, presents SGTE-compiled thermodynamic data for pure substances, including the elements in their stable states. The series now continues with a further 4 volumes of SGTE selected and compiled data – this time for binary alloy systems. For thermodynamic calculations involving alloy solution phases, Gibbs energies of the pure elements in different stable and metastable states are required. Such data have been compiled on behalf of SGTE by Dinsdale [91Din] and have recently been updated [02Din]. The values have found wide use internationally as the basis for thermodynamic assessments of higher order systems.

As with the pure element values, the binary alloy descriptions contained in the present 4-volume series are not only complete in themselves, but also extend the basis for thermodynamic assessments and calculations relating to multicomponent alloys.

Members of SGTE have played a principle role in promoting the concept of “computational thermochemistry” as a time and cost-saving basis for guiding materials development and processing in many different areas of technology. At the same time, through organisation of workshops and participation in CODATA Task Groups, SGTE members have contributed significantly to the broader international effort to unify thermodynamic data and assessment methods.

The SGTE data can be obtained via members and their agents world-wide for use with commercially available software developed by some of the members, to enable users to undertake calculations of complex chemical equilibria efficiently and reliably.

The SGTE Member organisations are:

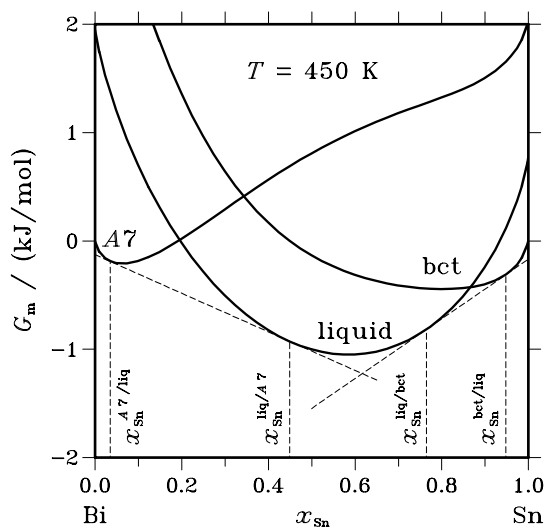
- Canada:** – THERMFACT LTD.LTEE
- France:** – Institut National Polytechnique (LTPCM), Grenoble  
– Association THERMODATA, Grenoble  
– IRSID, Maizières-lès-Metz  
– Université de Paris-Sud (EA 401)
- Germany:** – Rheinisch-Westfälische Technische Hochschule (MCh), Aachen  
– GTT-Technologies, Herzogenrath  
– MPI für Metallforschung (PML), Stuttgart
- Sweden:** – Royal Institute of Technology (MSE), Stockholm  
– Thermo-Calc Software AB, Stockholm
- United Kingdom:** – National Physical Laboratory (MATC), Teddington  
– AEA Technology plc, Harwell
- USA:** – The Spencer Group

## Assessment and selection procedures

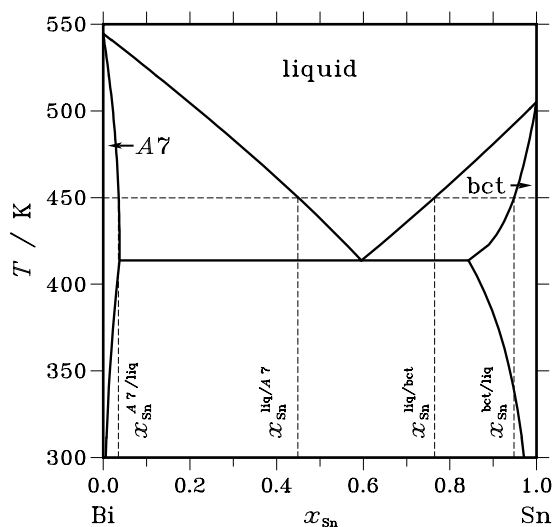
The assessments of the binary alloy systems presented in this 4-volume series have all been made using the so-called “CALPHAD method” [98Sau]. This method results in an optimised parametric description of the Gibbs energies of the phases of the system when taking into account the crystallographic structure of the phases and all the experimental thermodynamic and phase boundary data available. The thermodynamic

parameters provide a consistent analytical description of the phase diagram, chemical potentials, enthalpies of mixing, heat capacities, etc.

As an example, the relations between the Gibbs energy curves and the phase diagram for the Bi-Sn system are demonstrated in Figs. 1 and 2, respectively. In Fig. 1 the Gibbs energy curves for the phases in the Bi-Sn system are given as a function of the mole fraction of Sn,  $x_{\text{Sn}}$ , at  $T = 450$  K. At fixed pressure, temperature and composition, the equilibrium of the system is determined by the state with the lowest Gibbs energy. All equilibrium states are located on the convex hull of the set of G-curves which is constructed by applying double-tangents to the curves. The tangent points denote the boundaries between one- and two-phase regions. In Fig. 2, these points are marked on the selected isotherm of  $T = 450$  K. If this construction is repeated for other temperatures the complete phase diagram of the system is obtained.



**Fig. 1.** Gibbs energy functions for the phases in the Bi-Sn system at 450 K.



**Fig. 2.** Phase diagram for the system Bi-Sn.

If several published assessments are available for a particular system, selection has been made following an analysis of how well the available experimental data are reproduced by the description. Compatibility of the modelling used with respect to assembly of a data set for higher order systems has also been taken into account.

There are many different phases present in binary systems and, in order to combine their thermodynamic descriptions in higher order systems, it is important to know their crystal structures as well as the solubilities of alloyed elements in them. In these volumes, the naming of phases has been carried out as consistently as possible so as to facilitate identification of the same phase appearing in different binary systems.

The main characteristics of each system are presented in individual reports which generally include

- the calculated phase diagram
- an abstract summarising the main features of the system
- a summary of the various stable and metastable phases defined in the system together with crystallographic information, the phase name used in the database and the thermodynamic model used, including the occupation of the sublattices
- a table of the invariant reactions
- tables and diagrams with integral quantities
- tables and diagrams with partial quantities
- plots of calculated thermodynamic functions

### Criteria for selection of binary alloy assessments

In order to qualify for selection, the following information was reviewed:

- phase diagram
- thermodynamic information
- documentation
- models used for solution phases
- models used for stoichiometric phases
- feasibility of extrapolation
- compatibility with SGTE unary data

### Thermodynamic Modelling

#### Elements

The Gibbs energy of the pure element  $i$ ,  ${}^{\circ}G_i^{\phi}(T)$ , referred to the enthalpy for its stable state  $\phi$  at 298.15 K,  ${}^{\circ}H_i^{\phi}(298.15 \text{ K})$ , is denoted by  $\text{GHSER}_i$ . This quantity is described as a function of temperature by the following equation:

$$\begin{aligned} \text{GHSER}_i &= {}^{\circ}G_i^{\phi}(T) - {}^{\circ}H_i^{\phi}(298.15 \text{ K}) \\ &= a + b T + c T \cdot \ln T + d T^2 + e T^3 + f T^{-1} + g T^7 + h T^{-9} \end{aligned} \quad (1)$$

A number of temperature ranges may be used. The first and second derivatives of this quantity with respect to temperature are related to the absolute entropy and heat capacity of the compound at the same temperature. Experimental values for heat capacities can thus be directly used in the optimisation and will be related to the coefficients  $c, d, e, f, g$  and  $h$ .

For elements which have a magnetic ordering, e.g. Co, Cr, Fe, Ni and Mn, the term GHSER is referred to a para-magnetic state. An additional term is thus added to the molar Gibbs energy of the magnetic phase. For elements as well as for solutions, this term is equal to:

$$G^{\text{mag}} = RT \ln(\beta + 1) f(\tau) \quad (2)$$

where  $\tau$  is  $T/T^*$ ,  $T^*$  being the critical temperature for magnetic ordering (Curie temperature  $T_C$  for ferromagnetic materials or the Néel temperature  $T_N$  for antiferromagnetic materials), and  $\beta$  the average magnetic moment per atom of the alloy expressed in Bohr magnetons.

The function  $f(\tau)$  is given as:

$$\begin{aligned} \tau \leq 1 &: f(\tau) = 1 - [79\tau^{-1}/140p + (474/497)(1/p - 1)(\tau^3/6 + \tau^9/135 + \tau^{15}/600)]/A \\ \tau > 1 &: f(\tau) = -[\tau^{-5}/10 + \tau^{-15}/315 + \tau^{-25}/1500]/A \end{aligned}$$

with  $A = 518/1125 + (11692/15975)(1/p - 1)$ .

These equations were derived by Hillert *et al.* [78Hil] from an expression of the magnetic heat capacity  $C_p^{\text{mag}}$  described by Inden [81Ind].

The value of  $p$  depends on the crystal structure. For example,  $p$  is equal to 0.28 for fcc and hcp metals and 0.40 for bcc metals [81Ind]. For anti-ferromagnetic alloys the  $T^*$  and  $\beta$  are modelled as negative and they are divided by an *anti-ferromagnetic factor* of -1 for bcc and -3 for fcc and hcp before the values are used in equation (2).

For each element, equation (1) is taken from the SGTE unary database. These data have been published previously as the SGTE data for the pure elements by Dinsdale [91Din, 02Din].

The function  $\text{GHSEr}_i$  is also often used to express the thermodynamic functions of metastable structures  $\varphi$ , different from the stable structure of the pure element. The expression  ${}^\circ G_i^\varphi(T) - {}^\circ H_i^\phi(298.15 \text{ K})$  is equivalent to  ${}^\circ G_i^\varphi(T) - {}^\circ G_i^\phi(T) + \text{GHSEr}_i$ . The term  ${}^\circ G_i^\varphi(T) - {}^\circ G_i^\phi(T)$  is often called the lattice stability of element  $i$  in phase  $\varphi$ .

### Binary compounds

The Gibbs energy of the compound  $\text{A}_a\text{B}_b$  may be expressed as:

$$G_{\text{A}_a\text{B}_b}(T) - a {}^\circ H_{\text{A}}^\phi(298.15 \text{ K}) - b {}^\circ H_{\text{B}}^\phi(298.15 \text{ K}) = f(T) \quad (3)$$

where  $a$  and  $b$  are stoichiometric numbers. The expression for  $f(T)$  is identical to that given by equation (1).

Equation (3) can be transformed by applying equation (1) for each component

$$\begin{aligned} f(T) &= G_{\text{A}_a\text{B}_b}(T) - a {}^\circ G_{\text{A}}^\phi(T) - b {}^\circ G_{\text{B}}^\phi(T) + a \text{GHSEr}_{\text{A}} + b \text{GHSEr}_{\text{B}} \\ &= \Delta_{\text{f}} G_{\text{A}_a\text{B}_b}(T) + a \text{GHSEr}_{\text{A}} + b \text{GHSEr}_{\text{B}} \end{aligned} \quad (4)$$

The term  $\Delta_{\text{f}} G_{\text{A}_a\text{B}_b}(T)$  is the Gibbs energy of formation of the compound referred to the stable elements at temperature  $T$ . It can often be taken as a linear function of  $T$ .

### Gaseous species

An expression identical to equation (1) may be used to describe the Gibbs energy of the gaseous species with the additional  $RT \ln(P/P_0)$  term, where  $P$  is the total pressure and  $P_0$  the reference pressure, usually 0.1 MPa. The species in the gas phase are assumed to form an ideal solution. The reference state for each vapour species is taken to be the pure components at 0.1 MPa pressure. The thermodynamic properties of the gas species are normally obtained from vapour pressure measurements coupled to spectroscopic data. Data for gaseous substances are covered in more detail in subvolume (A) for pure substances.

Many species, i.e. molecules, may exist in the gas phase and each has a Gibbs energy of formation. The equilibrium within a gas for a given composition at a given temperature and pressure is calculated by minimising the Gibbs energy varying the fraction of the species. As the Gibbs energy is used as the modelling function in most solution databases it is not possible to calculate the critical point for gas/liquid. The models used for the different liquids are also not compatible with the ideal model for the gas.

### Condensed phases

The condensed phases can be divided into three groups.

#### 1: Substitutional solutions

For the substitutional solution  $\phi$ , the molar Gibbs energy is expressed as follows:

$$G_{\text{m}}^\phi = G_{\text{m}}^{\phi,\text{srf}} + G_{\text{m}}^{\phi,\text{id}} + G_{\text{m}}^{\phi,\text{E}} \quad (5)$$

with

$$G_{\text{m}}^{\phi,\text{srf}} = \sum_i x_i {}^\circ G_i^\phi \quad (6)$$

$$G_{\text{m}}^{\phi,\text{id}} = RT \sum_i x_i \ln x_i \quad (7)$$

$x_i$  is the molar fraction of component  $i$  with  $\sum_i x_i = 1$ . The term  $G_{\text{m}}^{\phi,\text{srf}}$  is the Gibbs energy of the phase relative to the reference state for the components and  $G_{\text{m}}^{\phi,\text{id}}$  is the contribution of ideal mixing entropy.

The Redlich - Kister equation [48Red], a power series expansion, is used to express the excess Gibbs energy,  $G_m^{\phi,E}$ , for the interaction between the two elements  $i$  and  $j$  as follows:

$$G_m^{\phi,E} = x_i x_j \sum_{\nu=0}^{\nu} {}^{\nu}L_{ij}^{\phi} (x_i - x_j)^{\nu} \quad (8)$$

The model parameter  ${}^{\nu}L_{ij}^{\phi}$  can be temperature dependent.

If experimental information for ternary solutions is available then an extra term can be added to equation (8). For a ternary system A–B–C, this term is equal to:

$$x_A x_B x_C L_{ABC} \quad (9)$$

The liquid is in most cases treated as a substitutional solution. For liquids with very strong short range order the associate model [78Som] or the ionic liquid model [85Hil] has sometimes been used.

For magnetic alloys, the composition dependence of  $T^*$  and  $\beta$  are expressed by:

$$T^*(x) = \sum_i x_i {}^{\circ}T_i^* + T^{*,E} \quad (10)$$

$$\beta(x) = \sum_i x_i {}^{\circ}\beta_i + \beta^E \quad (11)$$

where  $T^{*,E}$  and  $\beta^E$  are both represented by an expression similar to equation (8).

## 2: Ordered Phases

The use of the sublattice model, developed by Hillert and Staffansson [70Hil] based on Temkin's model for ionic solutions [45Tem] and extended by Sundman and Ågren [81Sun], allows a variety of solution phases to be treated, for example interstitial solutions, intermediate phases, carbides etc. All of these represent an ordering of the constituents on different sublattices.

As non-stoichiometric phases are formed by several sublattices, they can be schematically described as follows:

$$(A, B, \dots)_p (A, B, \dots)_q \dots$$

where the constituents A, B, ... can be atoms, vacancies, molecules or ions on the different sublattices ....  $p$ ,  $q$ , ... are the number of sites. If  $p + q + \dots = 1$ , then the thermodynamic quantities are referred to one mole of sites. Most often  $p$  and  $q$  are selected to be the smallest set of integers.

For each sublattice  $s$ , the site fraction of the species  $i$ ,  $y_i^s$ , is equal to

$$y_i^s = \frac{n_i^s}{\sum_j n_j^s} = \frac{n_i^s}{n^s} \quad \text{with} \quad \sum_i y_i^s = 1 \quad \text{and} \quad \sum_s n^s = n \quad (12)$$

where  $n_i^s$  is the number of species  $i$  in sublattice  $s$ ,  $n^s$  the number of sites in sublattice  $s$ , and  $n$  the total number of sites.  $n^s$  is related to  $n$  by  $n^s = n \cdot p / (p + q + \dots)$ . The number of sublattices and the species occupying them, is generally obtained from crystallographical information. The mole fraction of an element is obtained by

$$x_i = \frac{\sum_s n^s y_i^s}{\sum_s n^s (1 - y_{Va}^s)} \quad (13)$$

where  $y_{Va}^s$  is the fraction of vacant sites on sublattice  $s$ .

This model also describes stoichiometric phases, in which case the sublattices are occupied only by a single species, and substitutional phases which have a single lattice.

The molar Gibbs energy for a phase  $\phi$  expressed by the sublattice model is equal to

$$G_m^\phi = G_m^{\phi, \text{srf}} + G_m^{\phi, \text{id}} + G_m^{\phi, \text{E}} \quad (14)$$

As an example, a two sublattice phase with two elements A and B in each of the sublattices is considered. Denoting the sublattices with primes at the symbols, the surface of reference for the Gibbs energy is

$$G^{\text{srf}} = y'_A y''_A {}^\circ G_{A:A} + y'_A y''_B {}^\circ G_{A:B} + y'_B y''_A {}^\circ G_{B:A} + y'_B y''_B {}^\circ G_{B:B} \quad (15)$$

The terms  ${}^\circ G_{A:A}$  and  ${}^\circ G_{B:B}$  represent the Gibbs energies of the phase  $\phi$  for the constituent elements A and B. The colon separates the different sublattices. The terms  ${}^\circ G_{A:B}$  and  ${}^\circ G_{B:A}$  represent the Gibbs energies of the stoichiometric compounds  $A_p B_q$  and  $B_p A_q$ , which may be stable or metastable.  ${}^\circ G_{A:A}$ ,  ${}^\circ G_{B:B}$ ,  ${}^\circ G_{A:B}$  and  ${}^\circ G_{B:A}$  are numerically given by equations (3) and (1).

The term  $G_m^{\text{id}}$  is related to the molar configurational entropy and is equal to:

$$G_m^{\text{id}} = R T [p(y'_A \ln y'_A + y'_B \ln y'_B) + q(y''_A \ln y''_A + y''_B \ln y''_B)] \quad (16)$$

Finally, the excess Gibbs energy  $G_m^{\text{E}}$  is equal to

$$G_m^{\text{E}} = y'_A y'_B [y''_A L_{A,B:A} + y''_B L_{A,B:B}] \\ + y'_A y''_B [y'_A L_{A:A,B} + y'_B L_{B:A,B}] \\ + y'_A y'_B y''_A y''_B L_{A,B:A,B} \quad (17)$$

The terms  $L_{i,j:i}$  and  $L_{i:i,j}$  represent the interaction parameters between the atoms on one sublattice for a given occupancy of the other, and can be described by a Redlich - Kister polynomial, as follows:

$$L_{i,j:i} = \sum_{\nu=0} (y'_i - y'_j)^\nu {}^\nu L_{i,j:i} \quad (18)$$

The parameters  ${}^\nu L_{i,j:i}$  can be temperature dependent. The term  $L_{i,j:i,j}$  is known as the reciprocal parameter which may be related to the exchange reaction of A and B between the sublattices. It is usually assumed to be composition independent but may depend on temperature.

The above equations can easily be extended to ternary and higher order systems.

### 3: Phases with order-disorder transformation

Phases with order-disorder transformation, like  $A_2/B_2$  and  $A_1/L_1$  can also be described with the sublattice method although this disregards any explicit short range order contributions. A single Gibbs energy function may be used to describe the thermodynamic properties of both the ordered and disordered phases as follows:

$$G_m = G_m^{\text{dis}}(x_i) + \Delta G_m^{\text{ord}}(y_i^s) \quad (19)$$

where  $G_m^{\text{dis}}(x_i)$  is the molar Gibbs energy of the disordered phase, given by equation (5) and  $\Delta G_m^{\text{ord}}(y_i^s)$  is the ordering energy given by:

$$\Delta G_m^{\text{ord}} = G_m^{\text{subl}}(y_i^s) - G_m^{\text{subl}}(y_i^s = x_i) \quad (20)$$

where  $G_m^{\text{subl}}(y_i^s)$  is given by equation (14). This must be calculated twice, once with the original site fractions  $y_i^s$  and once with these site fractions replaced by the mole fractions. If the phase is disordered the site fractions and mole fractions are equal and thus  $\Delta G_m^{\text{ord}}$  equal to zero.

To ensure stability of the disordered phase, the first differential of  $G_m^{\text{subl}}$  with respect to any variation in the site occupancy must be zero at the disordered state. This enforces some relations between the parameters in  $G_m^{\text{subl}}$  as is discussed in [88Ans].

## Description of the Tables and Diagrams

The diagrams and tables which are presented for the binary systems provide an overview of the major thermodynamic properties and the mixing behaviour of these systems. Depending on the nature of the respective system, the number and the type of the presented diagrams and tables varies. For all systems, a calculated phase diagram, a short abstract and a table listing the condensed phases are provided. Additional tables and diagrams present data for invariant reactions, integral and partial quantities of the liquid and solid phases, and standard reaction quantities of intermetallic compounds in the system.

The following list gives an overview of the quantities in the tables and diagrams and their designations. The definition of these quantities is provided in the following paragraphs.

Symbol	Unit	Quantity
$a_A$		thermodynamic activity of the component A in a liquid or solid solution
$\Delta_f C_P^\circ$	J mol <sup>-1</sup> K <sup>-1</sup>	change of the molar heat capacity at constant pressure upon formation of a compound
$\Delta C_P$	J mol <sup>-1</sup> K <sup>-1</sup>	change of the molar heat capacity at constant pressure upon formation of a liquid or solid solution
$\Delta G_m$	J mol <sup>-1</sup>	integral Gibbs energy of a liquid or solid solution
$G_m^E$	J mol <sup>-1</sup>	integral excess Gibbs energy of a liquid or solid solution
$\Delta G_A$	J mol <sup>-1</sup>	partial Gibbs energy of the component A in a liquid or solid solution
$G_A^E$	J mol <sup>-1</sup>	partial excess Gibbs energy of the component A in a liquid or solid solution
$\Delta_f G^\circ$	J mol <sup>-1</sup>	standard Gibbs energy of formation of a compound
$\Delta H_m$	J mol <sup>-1</sup>	integral enthalpy of a liquid or solid solution
$\Delta H_A$	J mol <sup>-1</sup>	partial enthalpy of the component A in a liquid or solid solution
$\Delta_f H^\circ$	J mol <sup>-1</sup>	standard enthalpy of formation of a compound
$\Delta_r H$	J mol <sup>-1</sup>	enthalpy of reaction per mole of atoms
$p_i$	Pa	partial pressure of species i
$\Delta S_m$	J mol <sup>-1</sup> K <sup>-1</sup>	integral entropy of a liquid or solid solution
$S_m^E$	J mol <sup>-1</sup> K <sup>-1</sup>	integral excess entropy of a liquid or solid solution
$\Delta S_A$	J mol <sup>-1</sup> K <sup>-1</sup>	partial entropy of the component A in a liquid or solid solution
$S_A^E$	J mol <sup>-1</sup> K <sup>-1</sup>	partial excess entropy of the component A in a liquid or solid solution
$\Delta_f S^\circ$	J mol <sup>-1</sup> K <sup>-1</sup>	standard entropy of formation of a compound
$T$	K	thermodynamic temperature
$T_C$	K	Curie temperature
$x_A$		mole fraction of component A in an alloy or compound
$\gamma_A$		activity coefficient of the component A in a liquid or solid solution

The first diagram shows the phase diagram of the system. The single-phase fields and the compounds are marked with labels which are used in the tables to refer to the respective phases. All boundaries between phases which transform into each other by first-order transformations are drawn with solid lines. Second-order phase transformations and magnetic transformations are denoted by dashed and dotted lines, respectively.

The table “phases, structures and models”, contains crystallographic data and information on the thermodynamic model in the database. The designations of the phases according to Strukturbericht, prototype, Pearson symbol and the space group have been collected from various sources, including the original publication of the assessment and the reference books of Pearson [85Vil], Massalski [90Mas] and Smithells [92Bra]. The SGTE name is used by the accompanying software on the CD-ROM. The last column of this table denotes how the sublattices of the crystals have been mapped into a thermodynamic model. The species which dissolve in a common sublattice are enclosed in parentheses. The indices denote the stoi-

chiometric coefficients of the respective sublattices. If a sublattice is occupied by a single species only, the parentheses have been omitted. Vacancies are denoted by a box ( $\square$ ).

The table of “invariant reactions” provides detailed data for the invariant equilibria and special transition points shown in the phase diagram. For each of these reactions the temperature and the phase compositions are provided. The compositions of the participating phases are listed in the same sequence as given by the symbolic equation. The last column gives the reaction enthalpy on cooling for one mole of atoms according to the respective transformation.

The thermodynamic quantities for the liquid and solid solutions are provided by a set of three tables which are denoted by a suffix a–c after the Roman number. The first of these tables lists the integral quantities as well as the change of the molar heat capacity. The other two tables give the partial quantities for the respective two components.

The integral and partial quantities can often be obtained easily from experiments. Partial molar quantities are used to describe the thermodynamic behaviour of the individual components. In a binary system, the partial molar Gibbs energy  $G_A$  of component A can be calculated from the molar Gibbs energy,  $G_m$ , at constant temperature and pressure by the well-known relation:

$$G_A = G_m + (1 - x_A)(\partial G_m / \partial x_A)_{P,T} \quad (21)$$

$G_A$  is also known as the chemical potential of component A and denoted by the symbol  $\mu_A$ . Similar relations hold for the partial molar enthalpy,  $H_A$ , and the partial molar entropy,  $S_A$ .

Partial quantities provide the difference between the values of thermodynamic functions of a component in a solution and the corresponding values for the pure components. Thus, the partial Gibbs energy  $\Delta G_A$  of component A is calculated from  $G_A$  in the solution and  $G_A^\circ$  in the pure substance by:

$$\Delta G_A = G_A - G_A^\circ \quad (22)$$

Usually, the values of the pure components are given for their most stable modification at the respective temperature and pressure. But in order to avoid ambiguities the reference states for each component are given at the tables. The quantities  $\Delta H_A$  and  $\Delta S_A$  are defined accordingly.

The thermodynamic activity  $a_A$  of a component A is closely related to the partial Gibbs energy by:

$$a_A = \exp(\Delta G_A / RT) \quad (23)$$

Therefore, the activity is 1 for pure components in the chosen reference state.

The integral Gibbs energy,  $\Delta G_m$  is equal to the difference between the Gibbs energy of one mole of a solution  $G_m$  and the sum of the molar Gibbs energies of the pure components  $G_i^\circ$  at the same temperature and pressure. For a binary system the integral Gibbs energy is:

$$\Delta G_m = G_m - x_A G_A^\circ - x_B G_B^\circ \quad (24)$$

If the reference state of the components is the same phase as the mixture,  $\Delta G_m$  is also called the Gibbs energy of mixing. If the reference state of at least one component is different from the phase of the mixture then  $\Delta G_m$  contains the difference in Gibbs energies for the pure components between two phases. In these cases  $\Delta G_m$  is called the Gibbs energy of formation of the mixture. The quantities  $\Delta H_m$  and  $\Delta S_m$  are defined accordingly.

The excess quantities describe the deviation of the mixture from the ideal mixing behaviour. The molar excess Gibbs energy,  $G_m^E$ , is given by the difference of the integral Gibbs energy and the Gibbs energy of mixing for an ideal mixture:

$$G_m^E = \Delta G_m - G_m^{\text{id}} \quad (25)$$



In case of a simple substitutional solution,  $G_m^{\text{id}}$  is given by equation (7) and for solid solutions with several sublattices an expression similar to equation (16) applies.

The partial excess quantities can be derived from the integral excess functions by relations similar to those between partial and integral quantities. Thus, analogous to equation (21), the partial excess Gibbs energy of component A is given by:

$$G_A^E = G_m^E + (1 - x_A)(\partial G_m^E / \partial x_A)_{P,T} \quad (26)$$

Since the heat of mixing is zero for an ideal mixture, the excess enthalpy is identical to the heat of mixing and the partial excess enthalpy of a component is equal to its partial enthalpy. Therefore, the partial excess entropy can be calculated from the partial excess Gibbs energy by a temperature derivative or by the difference from the partial enthalpy:

$$S_A^E = -(\partial G_A^E / \partial T)_{P,x_A} = (\Delta H_A - G_A^E) / T \quad (27)$$

The activity coefficient is related to the partial excess Gibbs energy by an expression analogous to equation (23):

$$\gamma_A = \exp(G_A^E / RT) \quad (28)$$

For the case of simple substitutional solutions the activity of a component A is related to its mole fraction by:  $a_A = \gamma_A x_A$ .

The preceding equations describe the thermodynamic behaviour of a single phase. In an unconstrained equilibrium between two phases each component has the same chemical potential and the same activity in each phase and the integral quantities are linear functions of the composition in a two-phase region. In the diagrams, the functions are drawn with dashed lines in these regions.

Special considerations apply to stoichiometric compounds. Here, the partial quantities cannot be defined by the expression given in equation (21) because the composition cannot be varied. Instead, the chemical potentials are defined by the equilibrium with the next adjacent stable phase.

The table of “standard reaction quantities” provides the Gibbs energy, the enthalpy, and the entropy of formation for the given compounds from the pure elements in their most stable state at 298.15 K and 0.1 MPa. Phosphorus deviates from this rule since here the white modification is conventionally chosen as a reference state instead of the more stable red form. All values in this table are given for the reaction of a total amount of 1 mole of atoms.

## Description of the Software

The software provided with the volumes can calculate the printed phase diagrams but it also has some additional capabilities.

### Phase Names

The phase names are the same as used in the volumes. If the phase has a miscibility gap or could appear as both ordered and disordered in the same system, a “COMPOSITION SET” number is appended to the name after a hash sign. For example LIQUID and LIQUID#2 may appear as phase names if there is a miscibility gap in the liquid phase. Normally the composition set 1 is not identified explicitly. As both phases are thermodynamically identical the assignment of a specific composition set number is arbitrary. For ordering in the Au-Cu system for example there are four different composition sets for the FCC phase.

## Diagram Selection

The two basic windows for SGTEbin are shown in Fig. 3. In the text area of the base window references for data and other key textual information may appear. For the selection of a system press any two of the elements highlighted in bold print. The four buttons at the bottom of the window will become available. Four basic types of diagrams can be generated by use of specific buttons. These are,

- the phase diagram,
- the Gibbs energy curves for all phases as a function of composition at a specific temperature
- the activity curves of the two elements as a function of composition at a specific temperature
- a plot of the phase fractions as a function of the temperature for a given composition

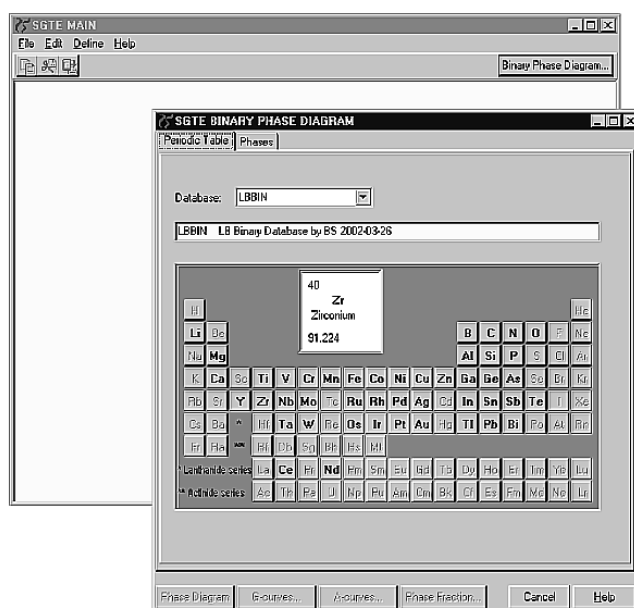


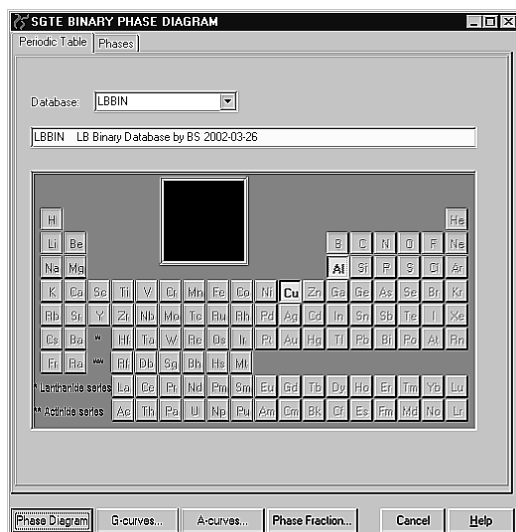
Fig. 3. Base window and periodic chart window.

The basic diagrams are obtained by just selecting two elements and the specific button. From these four calculations an infinite number of modified diagrams can be generated. Some of these will be discussed below.

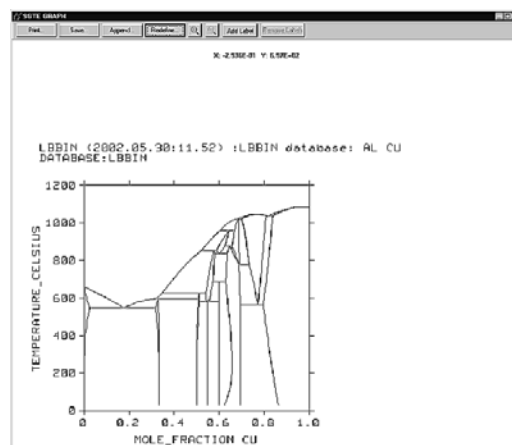
In addition to selecting the two elements one can also select the set of phases. The folder tagged "PHASE" gives the default selection of stable phases for the selected system. By changing this selection various metastable diagrams can be calculated.

## Phase Diagram

This button will generate a standard temperature - composition phase diagram with the axes in mole fractions and degrees Celsius, see the example in Fig. 4a and 4b. Magnifications and phase labels can be obtained using specific buttons in the graphical window. The REDEFINE button provides a menu, which will allow a change of the axes as shown in Fig. 5. Fig. 6 is equivalent to Fig. 4 but now plotted with activity and temperature in Celsius as axes variables.

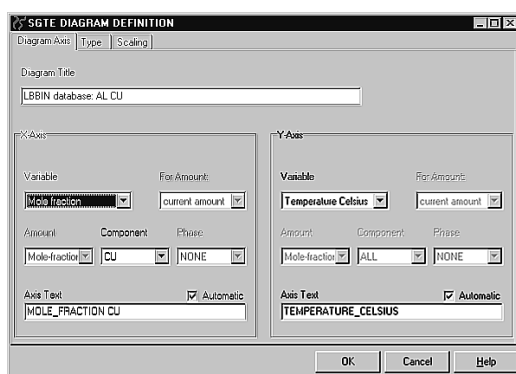


**Fig. 4a.** The periodic chart window shows the selected elements in red. Note that the buttons in the lower area are activated.

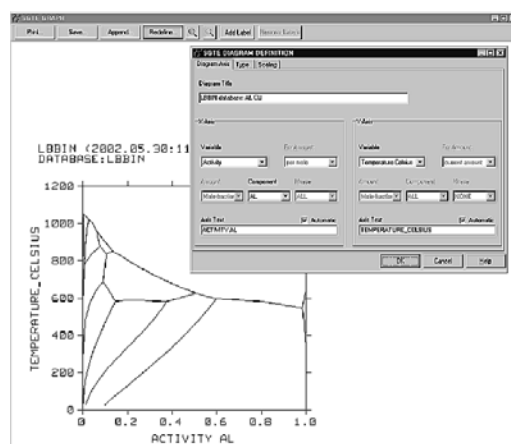


**Fig. 4b.** A binary phase diagram, here Al-Cu.

There are a number of different possible choices for the axis variable, some will be more sensible than others for a particular phase diagram. You may find it instructive to try a few on your own.



**Fig. 5.** The REDEFINE window for Al-Cu.



**Fig. 6.** The calculated Al-Cu system using the activity of Al and the Celsius temperature as axis variables.

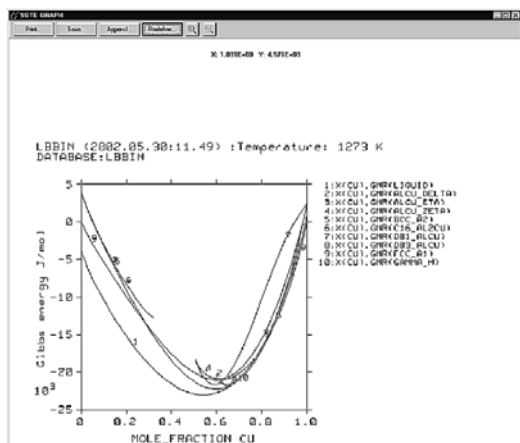
## G-Curves

In this diagram the Gibbs energies for each phase will be plotted vs composition at a given temperature. This diagram is related to the phase diagram in that the stable combination of phases is given by the lowest Gibbs energy at each composition. An example is given in Fig. 7. The number listed to the right of the diagram identifies each curve. Some phases have limited ranges of existence and stoichiometric phases appear with a small + sign. It is possible to change the axis to plot any integral quantity such as the enthalpy or entropy of the phases. In most cases the default for the reference phase for each element is the stable phase at 298.15 K.

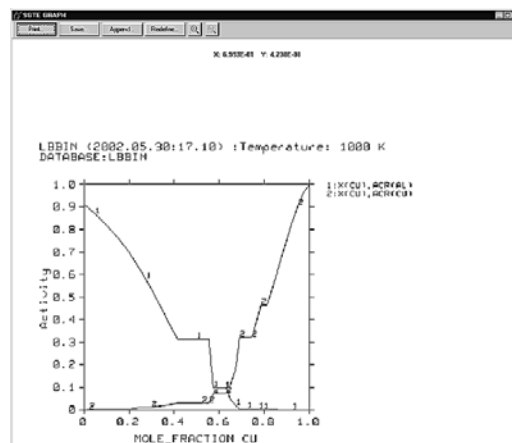
## A-Curves

In this diagram the activities of the two elements are plotted vs composition at a given temperature as shown in Fig. 8. The horizontal lines represent two-phase equilibria. It may be useful to change the activity axis to a logarithmic scale in the REDEFINE window or to plot the chemical potential instead. In most cases the default for the reference phase for each element is the stable phase at 298.15 K.

Note the difference between A-CURVES and G-CURVES. In the latter all phases are calculated for their range of composition. In the A-CURVES diagram the phases are included only where they are stable.



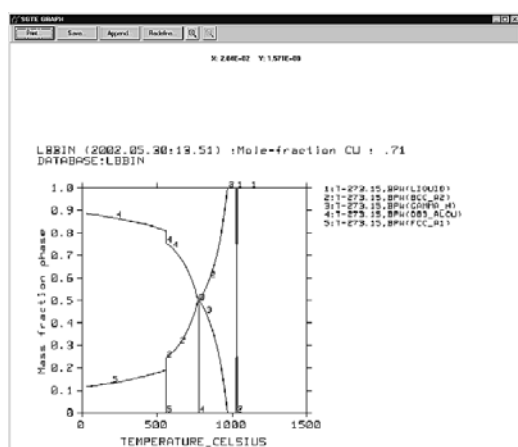
**Fig. 7.** The diagram calculated by pressing the G curves button. The Gibbs energy curves are shown for all phases of the Al-Cu system at 1273 K.



**Fig. 8.** The diagram calculated by pressing the A curves button. The component activities in the system Al-Cu are shown at 1000 K.

## Phase Fraction

This diagram gives the amount of the stable phases as a function of temperature for a given composition as shown in Fig. 9. The amount is given as mass fraction of phase. If one is interested to know how the amount of the phases varies with composition for a given temperature one can use the A-CURVES button and then change the axis with REDEFINE.



**Fig. 9.** The diagram calculated by pressing the phase fraction button. The curves show the amount of phase as function of the temperature at a given composition; the mole-fraction of copper is set to 0.71.

## Features and Errors

Unfortunately all software has errors. If you find a problem with the software please provide details by sending an email to [info@thermocalc.se](mailto:info@thermocalc.se). Please provide the minimum number of actions needed to reproduce the error. If you would like to suggest an additional feature send an email to the same address. One known problem may occur in the calculation of metastable phase diagrams where there may be a miscibility gap.

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