Comparison between Sn–Ni–Zn liquid phase thermodynamic assessments performed by the CALPHAD method and by geometrical models

Primerjava med termodinamskim ovrednotenjem taline Sn–Ni–Zn z metodo CALPHAD in geometrijskimi modeli

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Abstract: Estimation of the thermodynamic properties of the Sn–Ni–Zn systems has been performed using the general solution model and by other geometric models. Description of the ternary liquid phase (Gibbs excess energy dependence on the temperature and the composition) was achieved using the available thermodynamic data of the constitutive binary systems (Ni–Zn, Sn–Zn, Sn–Ni). The validity of the geometric models was checked. The calculations have been performed in a wide temperature range (1000–2000 K). The calculated quantities were compared with the available literature data. Good agreement of the present assessment with thermodynamically optimized values of the system Sn–Ni–Zn (obtained by the CALPHAD approach) was observed.

Povzetek: Termodinamske lastnosti sistema Sn–Ni–Zn smo ovrednotili z uporabo splošnega modela raztopin in z drugimi geometrijskimi modeli. Ternarno talino (odvisnost presežne Gibbsove energije od temperature in kemijske sestave) smo opisali z uporabo dostopnih termodinamskih podatkov iz robnih binarnih sistemov (Ni–Sn, Sn–Zn in Sn–Ni). Preverili smo tudi veljavnost geometrijskih modelov. Izračune smo izvedli v širokem temperaturnem območju (1000−2000 K). Izračunane vrednosti smo primerjali s podatki iz literature. Rezultati tega ovrednotenja se dobro ujemajo s termodi-

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namsko optimiranimi vrednostmi za sistem Sn–Ni–Zn, izračunani-
mi po metodi CALPHAD.

Key words: Sn–Ni–Zn system, liquid phase thermodynamics, general so-
lution model, ternary interaction parameters

Ključne besede: sistem Sn–Ni–Zn, termodinamika talin, splošni model
raztopin, ternarni interakcijski parametri

INTRODUCTION

The Sn–Ni–Zn system is interesting
as a potential lead-free solder material
because of the termination of lead-con-
taining solders industrial application is
envisaged, due to the high lead toxicity.
That is why the development of lead-
free solders is a current task. These
materials are expected to be designed
on the bases of systems including low-
melting elements like tin alloyed with
zinc or/and bismuth. On the other side,
nickel metallization often appears as
intrinsic part of the electronic devices.
Thus, investigations on a number of re-
lated solder/nickel systems and the cor-
responding properties were reported in
the literature[1, 2] but the thermodynam-
ics of the system is still unknown.

The border-systems Ni–Sn[3–5] and Ni–
Zn[6–10] are complex but they have been
studied intensively. The binary system
Sn–Zn presents a simple eutectic reac-
tion.[11] These systems are included in
the thermodynamic database devel-
oped by the European concerted action
COST 531 and reliable thermodynamic
optimizations are available for them.[12]

Nevertheless, there is no data about the
thermochemical properties of the ter-
nary liquid phase required for further
thermodynamic optimization of the
system Sn–Ni–Zn. Thus, the task of the
present study is to apply different ways
to assess the thermochemical proper-
ties of the ternary melt Sn–Ni–Zn.

THEORETICAL FUNDAMENTALS OF THE ASSESSMENTS

The so called "geometric models" give
the possibility to predict the thermody-
namic properties of a ternary phase (in
this case – liquid) using data belonging
to the respective binary border systems.
In this work, assessments were made
by means of the most common classic
geometric models of KOHLER,[13] MUG-
GIANU,[14] TOOP[15] and HILLERT[16] as well
as by the newly-developed but promi-
nent, general solution model (GSM)
developed by CHOU.[17, 18]

HILLERT[16] classified the geometric
models as symmetrical (e.g.[13, 14]) and
asymmetrical (e.g.[15, 16]) while look-
ing for a more universal approach to

ternary properties prediction. Such a universal approach was recently developed by CHOU[17, 18] and successfully employed in a variety of cases (e.g. ref. [19–22]). Nevertheless, a brief description of the techniques used shall be done below.

As usually, the molar excess Gibbs energy (ΔG^E/(J mol^{-1})) of the ternary liquid phase was chosen as a parameter which values had to be calculated by various models and compared. This quantity describes the contribution of the non-ideal mixing to the thermodynamic properties of a solution phase. The molar excess Gibbs energies values of all binary border-system (at a certain temperature and at specific compositions) are needed as starting points. These quantities were calculated by means of Thermocalc software package, using optimized parameters recently selected as result of the European concerted action for development of lead-free solders COST 531.[12]

In agreement with Redlich-Kister formalism, the composition dependence of the binary Gibbs molar excess energies (ΔG^E_{ij}) is given by the expression:

$$\Delta G^E_{ij} = X_i X_j (A^0_{ij} + A^1_{ij}(X_i - X_j) + A^2_{ij}(X_i - X_j)^2 + ... + A^n_{ij}(X_i - X_j)^2) \quad (1)$$

Here, A^o_{ij}, A^1_{ij}, A^2_{ij} are adjustable temperature dependent parameters belonging to the binary system "ij"; X_i and X_j indicate the mole fractions of the corresponding constituents.

The Gibbs molar excess energy of a ternary phase (ΔG^E_{123}), consisting of elements 1, 2 and 3, is given by the expression:

$$\Delta G^E_{123} = X_1 X_2 \Delta G^E_{12} + X_2 X_3 \Delta G^E_{23} + X_3 X_1 \Delta G^E_{31} + \Delta G^E_{123} \quad (2)$$

where ΔG^E_{12}, ΔG^E_{23} and ΔG^E_{31} can be obtained as defined above (equation 1) and ΔG^E_{123} is the contribution of the ternary non-ideal mixing. In the simplest case of a regular ternary solution it may be assessed by means of Equation (3):

$$\Delta G^E_{123} = X_1 X_2 X_3 A_{123} \quad (3)$$

where A_{123} is a ternary interaction parameter that might be temperature and concentration dependent.

The most essential equations, associated to the geometrical models[13–16] are only shown below only, because a detailed presentation would be out of the scope of this work. Thus, in a general case, a ternary system with constituents 1, 2 and 3 is considered where X_1, X_2 and X_3 are the mole fractions of the respective components. The molar excess Gibbs energies of the ternary liq-

uid phase (at a specific composition, temperature and pressure,) are estimated by means of equations 4–7 according to the authors,[13–16] in the same order:

$$\Delta G_{123}^E = \Delta G_{12}^E (1-x_3)^2 + \Delta G_{23}^E (1-x_1)^2 + \Delta G_{31}^E (1-x_2)^2 \tag{4}$$

$$\Delta G_{123}^E = \frac{X_1 X_2}{(X_1 + \frac{X_3}{2})(X_2 + \frac{X_3}{2})} \Delta G_{12}^E + \frac{X_2 X_3}{(X_2 + \frac{X_1}{2})(X_3 + \frac{X_1}{2})} \Delta G_{13}^E + \tag{5}$$

$$\frac{X_3 X_1}{(X_3 + \frac{X_2}{2})(X_1 + \frac{X_2}{2})} \Delta G_{13}^E$$

$$\Delta G_{123}^E = \frac{X_2}{1-X_1} \Delta G_{12}^E + \frac{X_3}{1-X_1} \Delta G_{13}^E + (X_2 + X_3)^2 \Delta G_{23}^E \tag{6}$$

$$\Delta G_{123}^E = \frac{X_2}{1-X_1} \Delta G_{12}^E + \frac{x_3}{1-x_1} \Delta G_{13}^E + \frac{x_2 x_3}{v_{23} v_{32}} \Delta G_{23}^E \tag{7}$$

In equations 4–7, the following symbols are represented: ΔG_{123}^E – Gibbs molar excess energy of the ternary liquid phase; ΔG_{ij}^E – the respective values of the two-component liquid phases, where the subscript indexes indicate the considered binary system. The symbols v_{23} and v_{32} in equation (7) denote the mole fractions of the constituents 2 and 3 in the binary system 2–3. The values $1 - X_1$ and $1 - X_3$ are numerically equal in such a case.

Equation (3) will be used for introduction to the General solution model (GSM) of CHOU[17, 18]:

$$\Delta G_{123}^E = X_1 X_2 X_3 f_{123} \tag{8}$$

Here f_{123} is the ternary interaction coefficient, related to the Redlich-Kister ternary interaction parameters A_{ijk} $(f_{123} = X_1 \cdot A_{123}^0 + X_2 \cdot A_{123}^1 + X_3 \cdot A_{123}^2)$.

This parameter is assessed in the following way[17]:

$$f_{123} = (2\xi_{12} - 1)\{ A_{12}^2((2\xi_{12}-1)X_3 + 2(X_1 - X_2)) + A_{12}^1 \} + (2\xi_{23}-1)$$
$$\{ A_{23}^2((2\xi_{23}-1)X_1 + 2(X_2 - X_3)) + A_{23}^1 \} + (2\xi_{31}-1)\{ A_{31}^2((2\xi_{31}-1)X_2$$
$$+ 2(X_3 - X_1)) + A_{31}^1 \} \tag{9}$$

Here ξ_{ij} are "similarity coefficients", that are defined by the quantity η_i called - "deviation sum of squares":

$$\xi_{ij} = \eta_i / (\eta_i + \eta_j) \qquad (10)$$

According to this model (GSM) the values of η_i are explicit functions of ΔG^E_{ij}, and are easily calculated when the adjustable coefficients of the three binary end-systems are known.

Basic thermodynamic information on the constitutive subsystems, needed for the assessment, was taken from ref.[12] For the Ni–Sn liquid phase updated parameters were used.[24] Actually, the optimized Redlich-Kister parameters of each system (Table 1) are essentially needed. They are used for the calculation (equations 4–8) of the molar excess Gibbs energies of the binary border-systems liquid phases. The following sequence of components was adopted for the calculations: Ni – 1, Sn – 2 and Zn – 3.

RESULTS AND DISCUSSION

Calculations of the coefficients f_{123} were done along three sections of the Ni–Sn–Zn system with molar Sn vs Zn ratios 1/3, 1/1 and 3/1 in the interval 1000–2000 K, at nickel molar fractions equal to 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1. In such a way a huge amount of information was obtained and used thereafter to derive the parameters A_{ijk}. For this purpose programming of Excel was used. The results are shown in Table 2.

Table 1. Optimized parameters (A°_{ij}, A^1_{ij}, A^2_{ij}) for the liquid binary phases of the Ni–Sn[24], Ni–Zn[12] and Sn–Zn[12] systems used in the present work; T/K – temperature.

System, $i-j$	$A^{\circ}_{ij}(T)$ J/mol	$A^1_{ij}(T)$ J/mol	$A^2_{ij}(T)$ J/mol
Ni–Sn (1–2)	$-106102.87 + 197.9089 \cdot T$ $-21.9959 \cdot T \cdot LN(T)$	$-29342.17 + 52.5528 \cdot T$ $-6.46094 \cdot T \cdot LN(T)$	$+1582.3$
Ni–Zn (1–3)	-50721.64 $+7.34178 \cdot T$	$+8436.3$ $+1.97211 \cdot T$	-25136.08 $+11.79211 \cdot T$
Sn–Zn (2–3)	$+19314.64 - 75.89949 \cdot T$ $+8.751396 \cdot T \cdot LN(T)$	-5696.28 $+4.20198 \cdot T$	$+1037.22$ $+0.98362 \cdot T$

Table 2. Ternary interaction parameters, A^v_{ijk}, for the Sn–Ni–Zn liquid phase obtained from the f_{123} coefficients. T/K – temperature.

System, ijk	$A^{\circ}_{ijk}(T)$ J/mol	$A^1_{ijk}(T)$ J/mol	$A^2_{ijk}(T)$ J/mol
Sn–Ni–Zn	$-884.2 + 6.5534 \cdot T$	$45415 - 18.16 \cdot T$	$-28292.6 + 17.82 \cdot T$

As already mentioned the binary integral Gibbs excess energies ought to be obtained initially. This was done by the Thermocalc software package, calculating binary activity values (referred to the liquid phases of the pure elements) at the pertinent points.

The ternary integral molar Gibbs excess energies assessed by the geometrical methods are graphically compared to those obtained by Thermocalc, using the optimized adjustable parameters of the border-systems only (Table 1). Sections with constant molar ratios between two of the components are plotted.

Results from a section with constant molar Sn/Zn equal to 1/3, at 1800 K are plotted in Figure 1. As one can see the curves 2 and 6 from one side and 1, 4 and 5 from the other side are grouped together, while the CALPHAD-type calculated values (curve 3) are situated between both groups. Surely, one has to bear in mind that curve 3 contains values assessed by binary parameters only. The asymmetrical methods (curves 4 and 5) give practically equal ΔG_{123}^{E} values while the quantities obtained by symmetrical methods (curves 1 and 6) differ significantly between each other. It should be noted that curve 6 (Muggiani model) is situated below all other curves at both other Sn/Zn ratios (1/1 and 3/1).

Figure 2 represents ternary integral molar Gibbs excess energies assessed along a molar Ni/Zn ratio equal to 1/3, at 1800 K. In this case, the values assessed by symmetrical methods (curves 1 and 6) are quite similar and are accompanied by the CALPHAD-type calculated quanti-
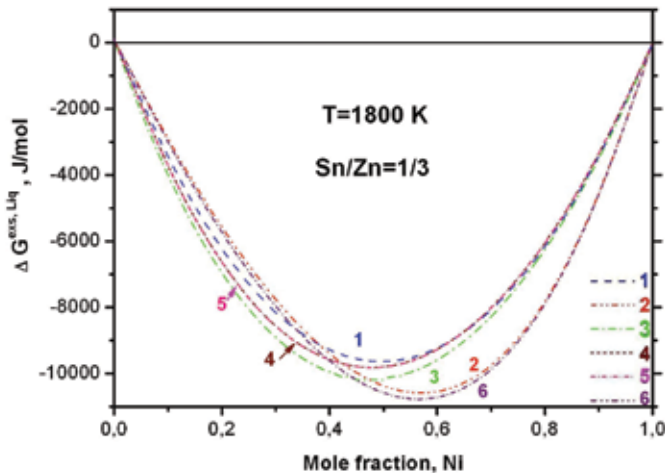

Figure 1. Molar Gibbs excess energies ($\Delta G^{ex,\,Liq}$, J/mol) of the liquid phase, along a section with constant molar Sn/Zn ratio equal to 1/3, at 1800 K calculated in this work according to various techniques: 1 – up to Kohler,[13] 2 – GSM,[34] 3 – CALPHAD (binary parameters only), 4 – Toop,[15] 5 – Hillert[16] and 6 – Muggianu.[14]

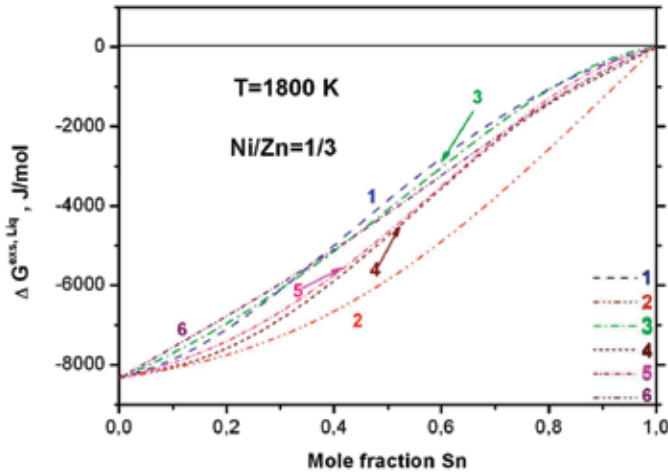**Figure 2.** Molar Gibbs excess energies ($\Delta G^{ex,\,Liq}$, J/mol) of the liquid phase, along a section with constant molar Ni/Zn ratio equal to 1/3, at 1800 K calculated in this work according to various techniques: 1 – up to KOHLER,[13] 2 – GSM,[34] 3 – CALPHAD (binary parameters only), 4 – TOOP,[15] 5 – HILLERT[16] and 6 – MUGGIANU.[14]

ties (curve). The same is valid for the values calculated by both asymmetrical methods (curves 4 and 5). The GSM–assessed integral molar Gibbs excess energies (curve 2) deviate from all others. Similar disposition of the considered curves is observed at the sections along molar Ni/Zn ratios equal to 1/1 and 3/1.

It can be seen in Figure 3 (ΔG_{123}^{E} values along Sn/Ni molar ratio equal to 1/3, at 1800 K, are plotted) that the curves 1–3, from one side and 4–6, from the other side, are rather close to each another. Thus, the type of the method (symmetric or asymmetric) does not play a decisive role regarding the values of the calculated ΔG_{123}^{E}.

The ΔG_{123}^{E} values assessed in various ways along the sections with Sn/

Ni molar ratios equal to 1/1 and 3/1 are roughly similar. The results for the ratio 3/1 are shown in Figure 4 in order to illustrate the shape of the curves.

In order to represent ΔG_{123}^{E} temperature dependence the values of the integral ternary molar Gibbs excess energies are plotted in Figures 5–7. The latter were calculated by GSM (by equations 9 and 10, using the parameters shown in Table 1) in the temperature range 1000–2000 K and along sections with Sn/Zn, Ni/Zn and Sn/Ni molar ratios equal to 1/1, respectively. Negative deviations from the Raoult's low are observed in general while in the regions rich of tin and zinc feeble positive ΔG_{123}^{E} are observed only.

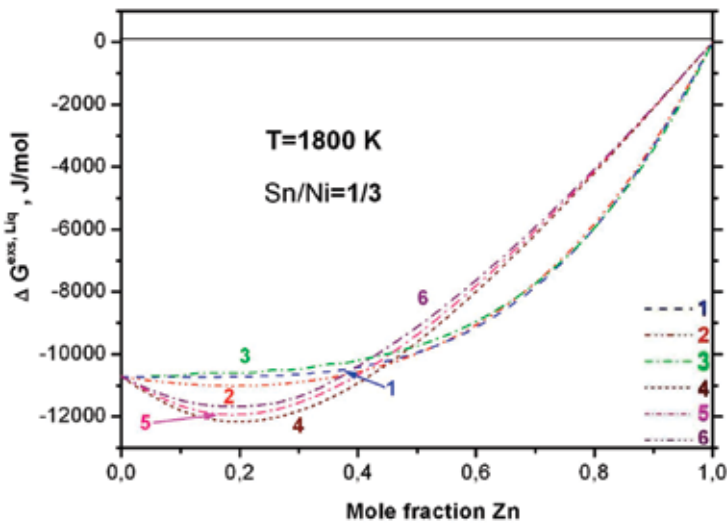**Figure 3.** Molar Gibbs excess energies ($\Delta G^{ex, Liq}$, J/mol) of the liquid phase, along a section with constant molar Sn/Ni ratio equal to 1/3, at 1800 K calculated in this work according to various techniques: 1 – up to Kohler,[13] 2 – GSM,[34] 3 – CALPHAD (binary parameters only), 4 – Toop,[15] 5 – Hillert[16] and 6 – Muggianu.[14]
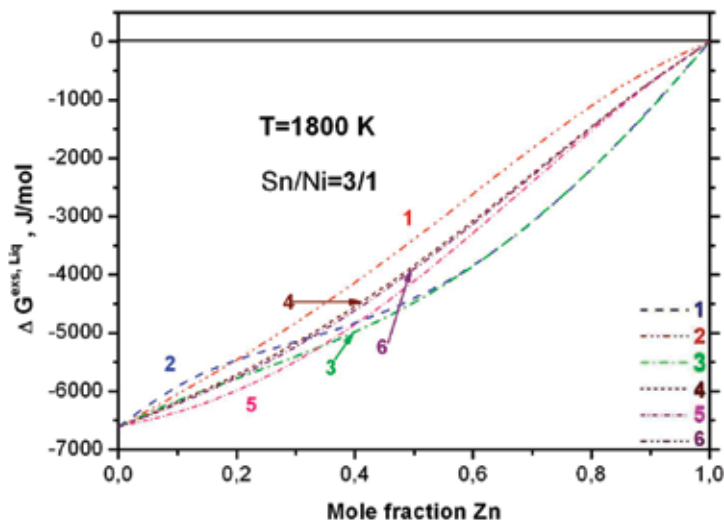

Figure 4. Molar Gibbs excess energies ($\Delta G^{exs, Liq}$, J/mol) of the liquid phase, along a section with constant molar Sn/Ni ratio equal to 3/1, at 1800 K calculated in this work according to various techniques: 1 – up to Kohler,[13] 2 – GSM,[34] 3 – CALPHAD (binary parameters only), 4 – Toop,[15] 5 – Hillert[16] and 6 – Muggianu.[14]
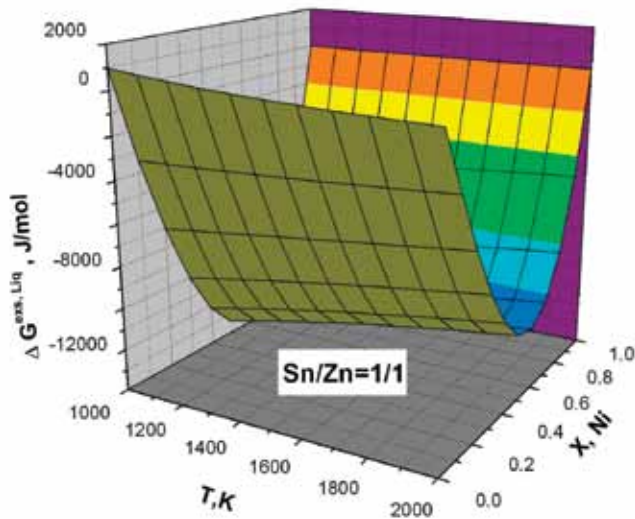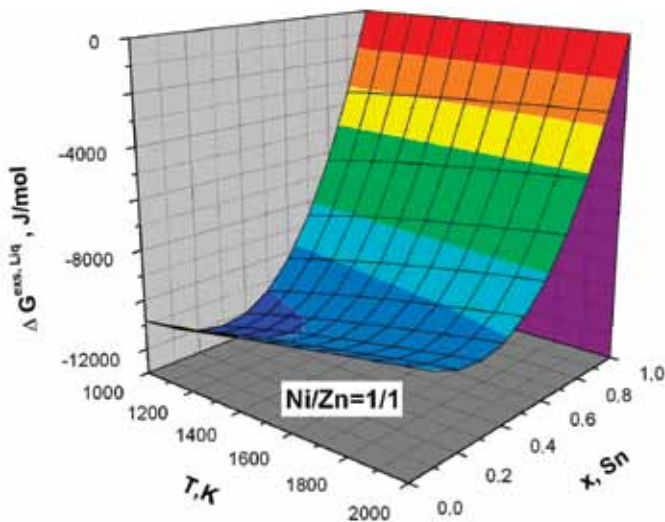
Figure 5. Calculated by GSM values of the integral ternary molar Gibbs excess energies in the temperature range 1000–2000 K. Section with Sn/Zn ratio equal to 1/1. $\Delta G^{ex, Liq}$, J/mol – molar Gibbs excess energy of the ternary liquid phase; x_{Ni} – nickel mole fraction; T/K – temperature.

Figure 6. Calculated by GSM values of the integral ternary molar Gibbs excess energies in the temperature range 1000–2000 K. Section with Ni/Zn ratio equal to 1/1. $\Delta G^{ex, Liq}$, J/mol – molar Gibbs excess energy of the ternary liquid phase; x_{Sn} – tin mole fraction; T/K – temperature.
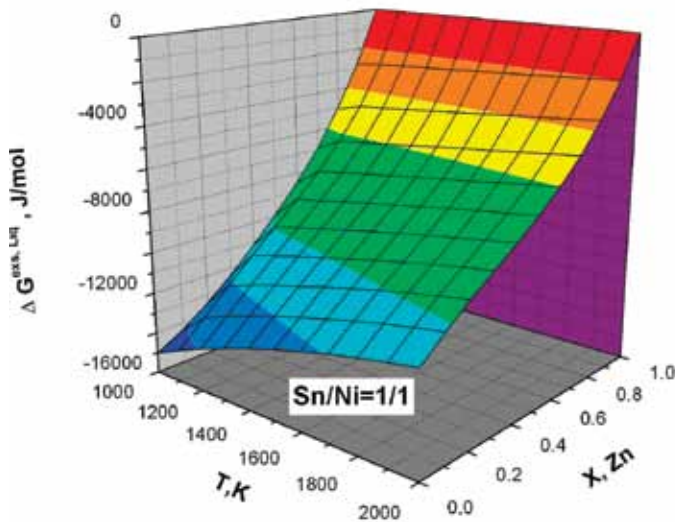
Figure 7. Calculated by GSM values of the integral ternary molar Gibbs excess energies in the temperature range 1000–2000 K. Section with Sn/Ni ratio equal to 1/1. $\Delta G^{ex, Liq}$, J/mol – molar Gibbs excess energy of the ternary liquid phase; x_{Zn} – zinc mole fraction; T/K – temperature.

Conclusions

Some thermodynamic properties of the Sn–Ni–Zn liquid phase were predicted using a general solution model developed by Chou, two symmetrical and two asymmetrical models. Redlich-Kister ternary interaction parameters of the liquid phase were assessed.

The values of the ternary liquid phase molar Gibbs excess energies assessed by geometric models were compared to those calculated by the CALPHAD method using binary optimized parameters only. Good mutual agreement was found indicating that the interaction parameters for the ternary system would have small values.

Acknowledgments

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