

THERMODYNAMIC DESCRIPTION OF THE BINARY CU-BI SYSTEM

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Abstract

The Cu-Bi alloys are important from a technological point of view. Copper-Bismuth alloys are part of lead-free solders that are being studied nowadays. A good thermodynamic description of this system is essential for further investigations of multi-components materials that include Cu and Bi. Due to the frequent use of Cu as a substrate material in electronics, it is of importance to understand the interactions between the solders materials and the substrate. A new assessment was proposed in this work based on multiple published experimental reports. Calculations of the thermodynamic properties have been carried out following the CALPHAD method, and using the ThermoCalc software. Good agreement between calculations and experimental data was found, and a new database considering the Cu-Bi alloy has been performed.



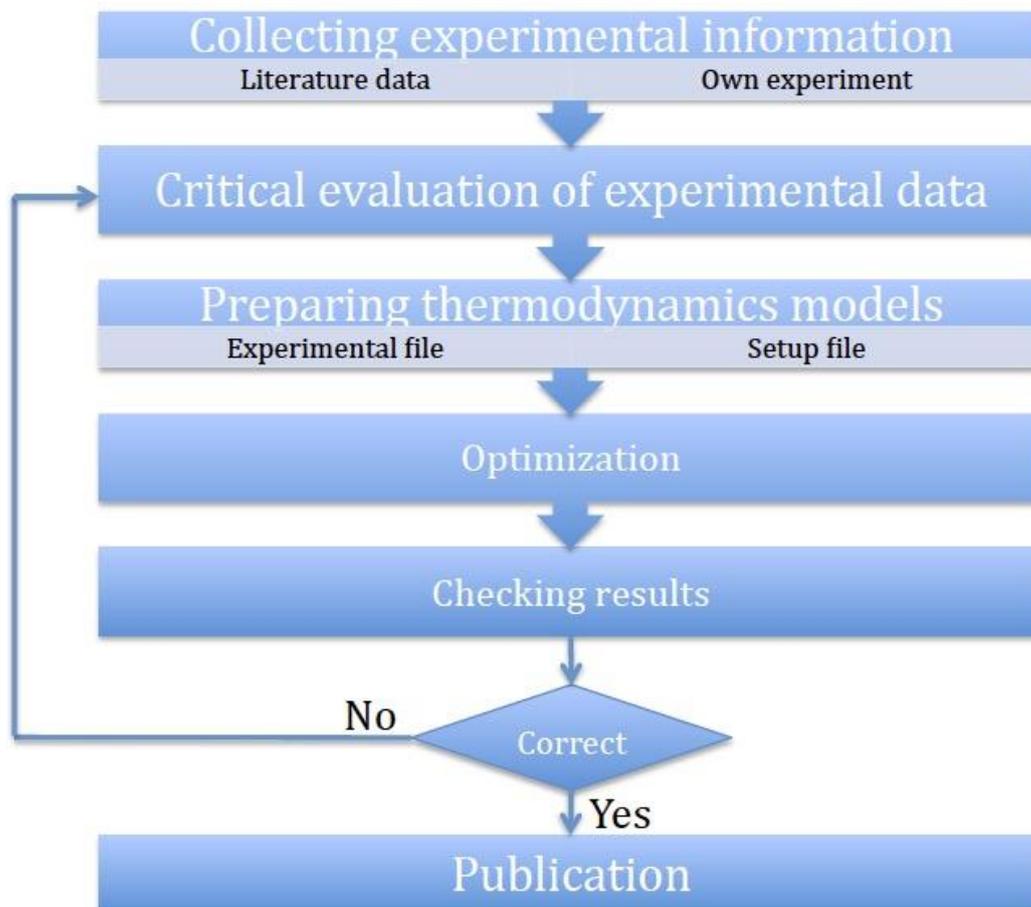
1. Introduction

The ROHS Directive of the European Union (“Directive on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment 2002/95/EC) became effective on 1 July 2006, with similar legislature active or impending in various other parts of the world. Due to this directive the use of lead is prohibited in electronic products, however, with a number of exemptions due to reliability issues. One of them concerns the use of high-lead containing Pb–Sn solders (with Pb contents considerably higher than the eutectic composition) for so called high-temperature soldering applications. This has initiated an extensive search for alternative alloy systems with melting temperatures higher than about 230 °C. As possible alternatives have been identified binary Ag–Bi or ternary Ag–Bi–Sn alloys. On the other hand, it has also been attempted to decrease the melting temperatures of Sn–Ag lead-free solders by adding small amounts of Bi. Due to the frequent use of Cu as a substrate material in electronics, it is of importance to understand the interactions between these solders and the substrate, based on a sound knowledge of the phase equilibria in the system Bi–Cu–Sn and the quaternary Ag–Bi–Cu–Sn system. [1]

One of the goals of the European COST Action 531 (“Lead-free Solder Materials”) has been the development of a thermodynamic database which contains the thermodynamic properties of various binary and ternary alloy systems, relevant for soldering, in a parametric form. Using commercially available standard software, the corresponding phase diagrams can be calculated based on the well-known CALPHAD method. [1]

2. Calphad Method

The CALPHAD (CALculation of PHase Diagram) method was established as a tool for treating thermodynamics and phase equilibria of multi-components system. It has become now a powerful method for a wide range of applications where modelled Gibbs energies and their derivatives are used to calculate properties and simulate phase transformations in real multicomponent materials. Since then the method has been successfully applied to diffusion mobility in multicomponent systems, creating the foundation for simulation of diffusion processes in these systems. Recently, CALPHAD method has been expanded to other phase-based properties, including molar volumes and elastic constants, and has the potential to treat electrical and thermal conductivity and even two-phase properties, such as interfacial energies. The CALPHAD approach is based on the fact that a phase diagram is a manifestation of the equilibrium thermodynamic properties of the system, which are the sum of the properties of the individual phases. It is thus possible to calculate a phase diagram by first assessing the thermodynamic properties of all the phases in a system.



3. Literature Review

3.1 Phase Diagram

Thermodynamic properties of liquid Cu–Bi alloys had been investigated in numerous research studies. The phase diagram is reasonably well known, the older data having been evaluated by Hansen and Anderko [2] and later refinements published in the current literature [3, 4]. According to these researches, the binary system of bismuth-copper is of a simple eutectic type with the eutectic point at about 270 °C, close to that of pure bismuth. The solid solubility of bismuth in copper is low, below 0.01% [Bi]_{Cu} in maximum, and the solubility of copper in solid bismuth is negligible. No stable intermetallic phases have been reported.

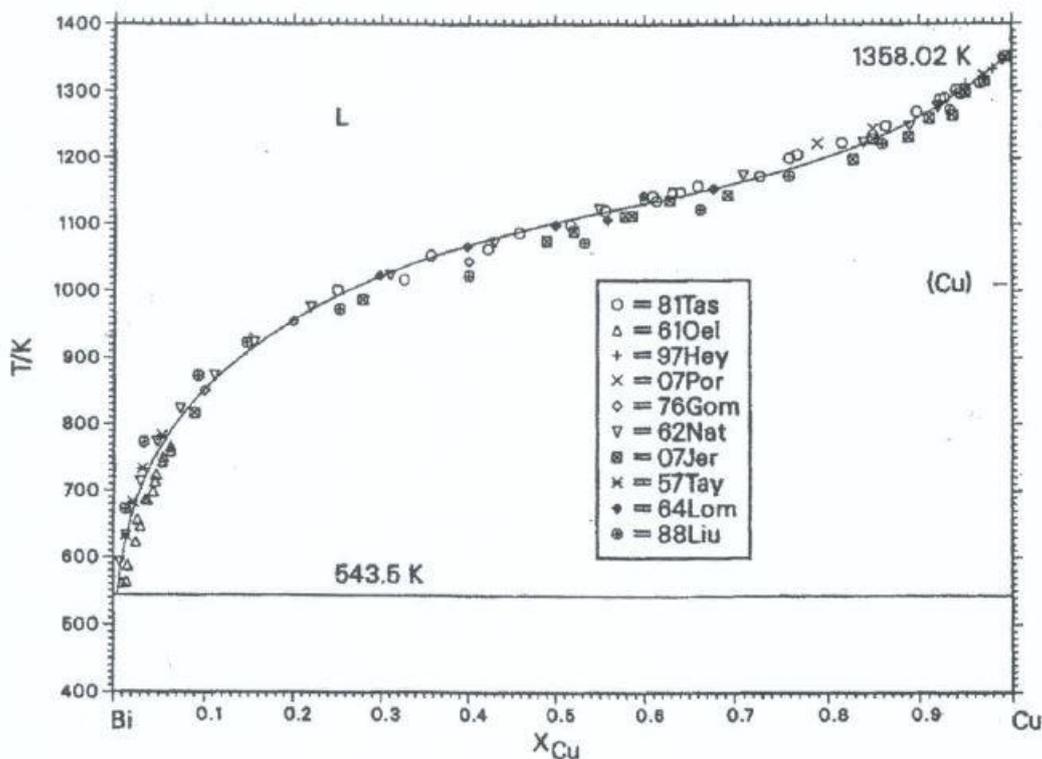


Figure 1. The calculated phase diagram for Bi-Cu at 400-1400 K for several authors.

Pure copper crystallizes at 1084.87 C in an FCC lattice which is stable down to room temperature. Bismuth solidifies at 271.44 C, crystallizing in a rhombohedral form [5].

3.2 Enthalpies of mixing

Several calorimetric investigations of the enthalpy of mixing of liquid Bi-Cu alloys can be found in the literature. In 1930, Kawakami [6] published the integral enthalpies of mixing at 1200 °C, although with a large scattering of the experimental values. Later, the binary system was investigated by Oelsen et al. [7] and Takeuchi et al. [8] at 1143 and 1342 °C, respectively. For Cu-rich alloys the results of the two latter investigations are in quite good agreement whereas significant lower enthalpy values were found by Takeuchi et al. [8] in the region towards Bi. On the other hand, Nikolskaya et al. [9] derived the enthalpy of mixing of liquid Bi-Cu alloys from their EMF measurements. All these authors found a maximum in the enthalpy of mixing, however, with different absolute values and at different compositions: 6900 J/mol at 60 at. % Cu [4], 6100 J/mol at 50 at.% Cu [7], 5600 J/mol at 59 at.% Cu [8] and 6800 J/mol at 60 at.% Cu [9]. In general, there is no indication for any significant temperature dependence of the enthalpies of mixing. There are two thermodynamic assessments of Bi-Cu in the literature, by Niemelä et al. [10] and Teppo et al. [5], both of the same research group. The enthalpies of mixing were calculated based on an optimized thermodynamic data set, and the calculated curves are nearly symmetrical with a maximum of about 6000 J/mol at 53 at.% Cu. The Cu-Bi system shows a strong tendency to form a liquid-state miscibility gap [10].

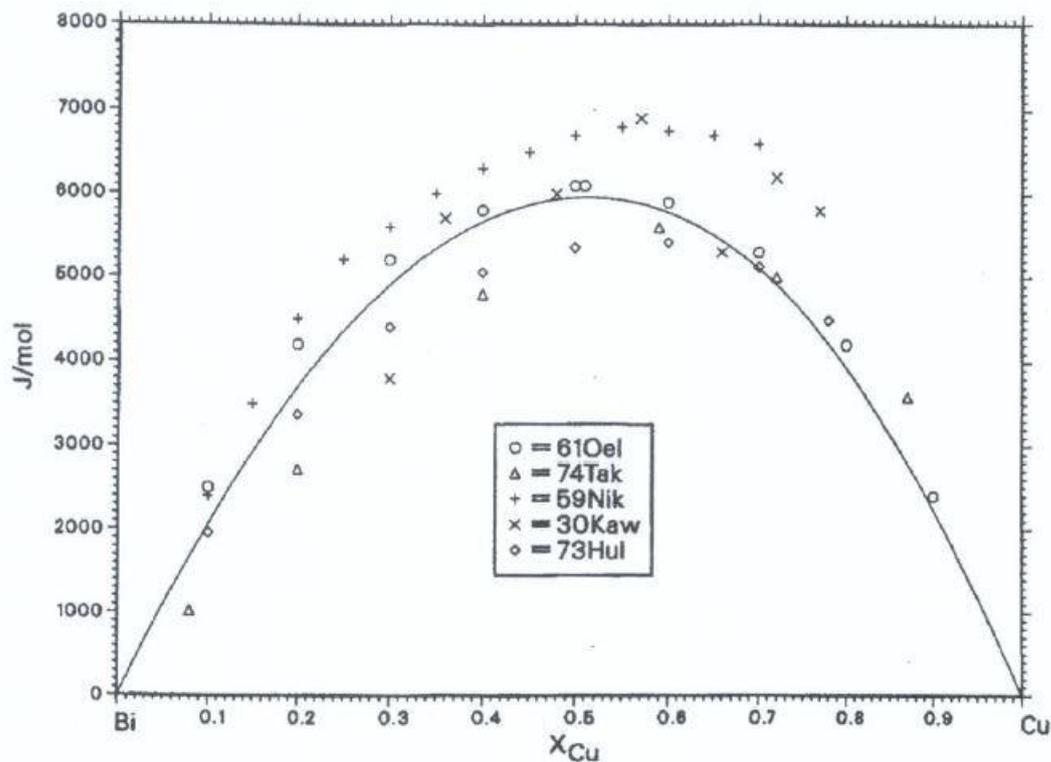


Figure 2. Integral enthalpy of mixing of the molten Bi-Cu alloys by multiple authors; standard states are Bi(l) and Cu(l).

3.3 Activities in liquid

Activity measurements of bismuth have been carried out by Teppo et al. [5] using a Kundsen effusion technique combined with an electrobalance. They reported systematically too low bismuth activity values in copper-rich alloys at 1373 K. They contrasted their calculations and experimental data with previous works by Nikolskaya et al. [9], Predel et al. [16], Azakami et al. [17] and Itoh. Not having a very good agreement with these last two. Taskinen et al. [19] also calculated activity of bismuth extrapolating the data from copper activity calculations using the Gibbs-Duhem equation. Their results are opposed to Teppo et al. [5], differing more with Nikolskaya [9] and Predel [16], but closer to Azakami et al. [17].

The phase diagram and the thermodynamic properties of the bismuth-copper binary system have been reassessed by using simultaneously experimental thermodynamic and phase diagram data from original studies for optimizing the adjustable parameters of the solution models.

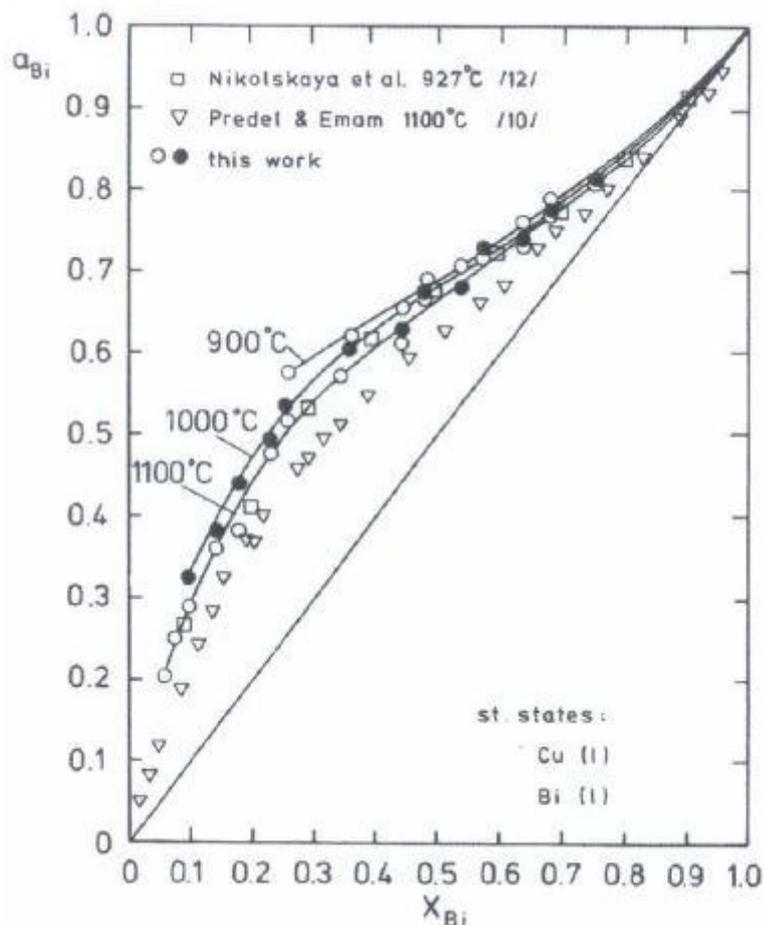


Figure 3. Activity of bismuth in liquid copper-bismuth alloys according to various authors; standard state is Bi(l)



4. Thermodynamic Model

This modelling of the binary Cu-Bi system includes 2 phases: FCC_A1 (Cu) and Rhombohedral_A7 (Bi).

The Gibbs energies of pure elements with respect to temperature ${}^0G_i(T) = G_i(T) - H_i^{SER}$ are represented by Equation 1:

$${}^0G_i(T) = a + bT + cT \ln(T) + dT^2 + eT^{-1} + fT^3 + iT^4 + jT^7 + kT^{-9} \quad (1)$$

The ${}^0G_i(T)$ data are referred to the constant enthalpy value of the standard element reference H_i^{SER} at 298.15 K and 1 bar as recommended by Scientific Group Thermodata Europe (SGTE) [11]. The reference states are Rhombohedral_A7 (Bi) and FCC_A1 (Cu). The expression is given for several temperature ranges, where the coefficients $a, b, c, d, e, f, i, j, k$ have different values. The functions are taken from SGTE Unary (Pure elements) TDB v5.0 [11].

Solid and liquid solution phases (FCC_A1, RHOMBOHEDRAL_A7, and Liquid) are described by the substitutional solution model [12]:

$$G_m(T) = \sum_i x_i^0 G_i(T) + RT \sum_i x_i \ln(x_i) + \sum_i \sum_{j>i} x_i x_j \left(\sum_v v_{Lij} (x_i - x_j)^v \right) \quad (2)$$

where the $\sum_i \sum_{j>i} x_i x_j (\sum_v v_{Lij} (x_i - x_j)^v)$ part is the Redlich–Kister polynomial for excess Gibbs free energy.



5. Procedure

The thermodynamic parameters for all phases in the system were optimized using ThermoCalc software [13]. For this optimization, thermodynamic data for the liquid and solid phases, invariant reactions and liquidus/solidus were used and optimization was done according to Shmid-Fetzer et al. [14] guideline. Each piece of the selected information was given a certain weight based on experimental uncertainty. The optimization was carried out step by step. First, the optimization of the liquid phase was performed, and then the solid phases were assessed. All parameters were finally evaluated together to provide the best description of the system. The calculated interaction parameters are shown in Table 3.

5.1 Data Optimisation

In a thermodynamic database, each phase in a system is characterised using a mathematical model of its Gibbs energy. The Gibbs energy of a phase depends on various state variables. It can be defined individually even in a heterogeneous system with many stable phases since the properties of one phase are completely independent of the properties of the other phases in the system. In most alloy systems, the thermodynamic properties of a phase can be modelled by expressing how the Gibbs energy depends on temperature and composition. State variables such as pressure, volume or entropy can also serve as parameters in the Gibbs energy expression. The Gibbs energy of the whole system is the sum of the products of the Gibbs energy of each phase multiplied by the amount of that phase.

How the Gibbs energy of the phase varies with various state variables is determined by a mathematical model and how various adjustable parameters of the model is set. By optimising these parameters, you can calculate the thermodynamic properties of a system under various conditions (by calculating phase diagrams for example). The thermodynamic properties themselves are functions of temperature, pressure or composition. They include, among other properties, standard enthalpy of formation, entropy, heat capacity, molar volume, thermal expansivity, compressibility and Curie temperature for magnetic transformations.

Data optimisation is about adjusting the model parameters so that calculated equilibria fit well with experimental data. An important part of a data optimisation is therefore collecting and assessing available experimental and theoretical information about phase equilibria and thermochemical properties of a system.

When you optimise the parameters of the model of a phase, you put what is called optimising variables into the Gibbs energy expressions of those parameters. During the optimisation, the values of these variables are varied in order to find a fit between the calculated equilibria and the experimental data that you base the optimisation on.



Once you have settled on a Gibbs energy expression for a certain parameter of a phase of the element, then you must stick to this expression in all future optimisations involving the element. If you do not do this, then you must re-optimize all previous systems that involve this element when the expression is changed.

The Thermo-Calc program allows you to optimize parameters that characterise not only binary systems, but also ternary system and systems of even higher orders. You can even optimize parameters that characterise systems of different orders at the same time.

5.2 The least-squares method

Data optimisation in Thermo-Calc is based on the least-squares method for fitting values calculated on the basis of a model with observed quantities. The Thermo-Calc program is accordingly trying to find the optimising variable values that lead the minimised sum of the squares of the differences between the calculated values and the observed quantities (that is, of the errors or residuals). The least-squares method works best under the following conditions:

- The observed quantities have a Gaussian probability distribution.
- The observed quantities are only subject to random errors.
- The different observations (experiments) are uncorrelated
- The standard deviation of each observation can be estimated.
- The number of observations is large.
- The models used give precise predictions.

Of course, these conditions are usually not all met in a normal thermodynamic assessment. But even in non-ideal conditions, there is no known method that works better than the least-squares method.

5.3 The CALPHAD approach

The data optimisation functionality in Thermo-Calc works according to the CALPHAD approach to computational thermodynamics. This approach builds on the development of models that accurately represent thermodynamic properties for various phases. These models enable you to predict the thermodynamic properties of multicomponent systems-based data concerning binary and ternary subsystems. The predictions can take many factors into accounts, such as, for example, crystallography, type of bonding, order-disorder transitions and magnetic properties. CALPHAD is originally an abbreviation of *CAL*culat*ion of PHA*se *Diagrams*, but as the approach has expanded in scope, it now stands for *computer coupling of phase diagrams and thermochemistry*.



5.4 Data Optimisation Workflow

When you carry out an optimisation using Thermo-Calc, you typically follow a workflow as outlined below.

1. Collect experimental data about your system from various sources such as journal articles and reports. The data that has been used is the one mentioned in the literature review.
2. Create a POP-file in which you enter the experimental data you have collected. It is critically important to make a proper evaluation of the data available. The experience of the authors, quality of experiments, contrast of the references and number of citations are some of the criteria to take into account when selecting data.

It is of vital importance to arrange all the data properly. The management and organization of the experimental data in the POP-file makes a big difference in the calculation, due to how it is done. Good arrangement by property, author, temperature and other characteristics pertinent in each case is important.

In Figure 4, an example is shown on how the POP-file looks like for a set of experimental data.

```

TABLE_HEAD 30
CREAT_NEW_EQUILIBRIUM @@,1
CHANGE_STATUS PHASE LIQUID=FIX 1
SET_REFERENCE_STATE BI LIQUID * 1E5
SET_REFERENCE_STATE CU LIQUID * 1E5
SET_CONDITION T=1400 P=1E5 X(LIQUID,CU)= @1
EXPERIMENT ACR(BI)= @2:0.01

TABLE_VALUES
0.236189      0.787761
0.376039      0.668577
0.388934      0.632613
0.407227      0.599091
0.5863         0.547497
0.586525      0.516249
0.595758      0.487469
0.79118        0.421571
0.791614      0.361478
0.800986      0.313469
0.891303      0.304505
0.891772      0.239604
0.89198        0.210759
TABLE_END
  
```

Figure 4. Example of set of data in POP-file for the Cu-Bi system



3. Create a setup macro file in which you define your system and the variables you want to optimise. A useful general procedure is to first find a minimum set of variables that allows you to calculate most of the experiments.

Figure 5 shows how the Gibbs functions are defined for this work, included in the setup-file.

```
ent-phase LIQUID , 1
  BI,CU ; N N

ent-param G(LIQUID,BI;0)          298.15 +GLIQBI; 3000 N
ent-param G(LIQUID,CU;0)          298.15 +GLIQU; 3200 N
ent-param G(LIQUID,CU,BI;0)       298.15 +V1+V2*T+V3*T*LN(T); 2000 N
ent-param G(LIQUID,CU,BI;1)       298.15 +V4+V5*T+V6*T*LN(T); 2000 N
ent-param G(LIQUID,CU,BI;2)       298.15 +V7+V8*T+V9*T*LN(T); 2000 N
```

Figure 5. Extract of the setup-file for the Cu-Bi system showing the definition of the Gibbs energy and the variables to optimize.

4. Run the setup macro file.

5. Compile your POP-file. This file often contains errors, which need to be corrected, and the file recompiled several times before the compilation is completed without errors.

6. In the ED_EXP module, check that the experiments in your POP-file reach equilibrium with reasonable results. If any experiments do not reach equilibrium with reasonable results, then try changing the starting values on equilibrium conditions (such as composition) to see whether the equilibrium can be computed after all. If this does not work, then you can temporarily exclude the experiment from the optimisation. At a later stage in the optimisation, when the optimising variables have different values, you can check whether the experiments can be computed with reasonable results.

7. Back in the PARROT module, run the first optimisation cycle and evaluate the feedback in the console. You can also plot diagrams in the POLY module that allow you to visually inspect the fit between calculated optimisation results and the experimental data. If you are not satisfied with the fit, then enter the ED_EXP module again and adjust the weights of the experiments in a way that is likely to improve the fit and run another optimisation cycle. Reiterate until you are satisfied with the fit.

8. Once you get the optimisation stable and smooth with the minimum set of variables chosen in step 3 above, try using different sets of variables to see whether improvements are possible.



Figure 6 shows the command lines for plotting calculated properties superimposed to experimental data.

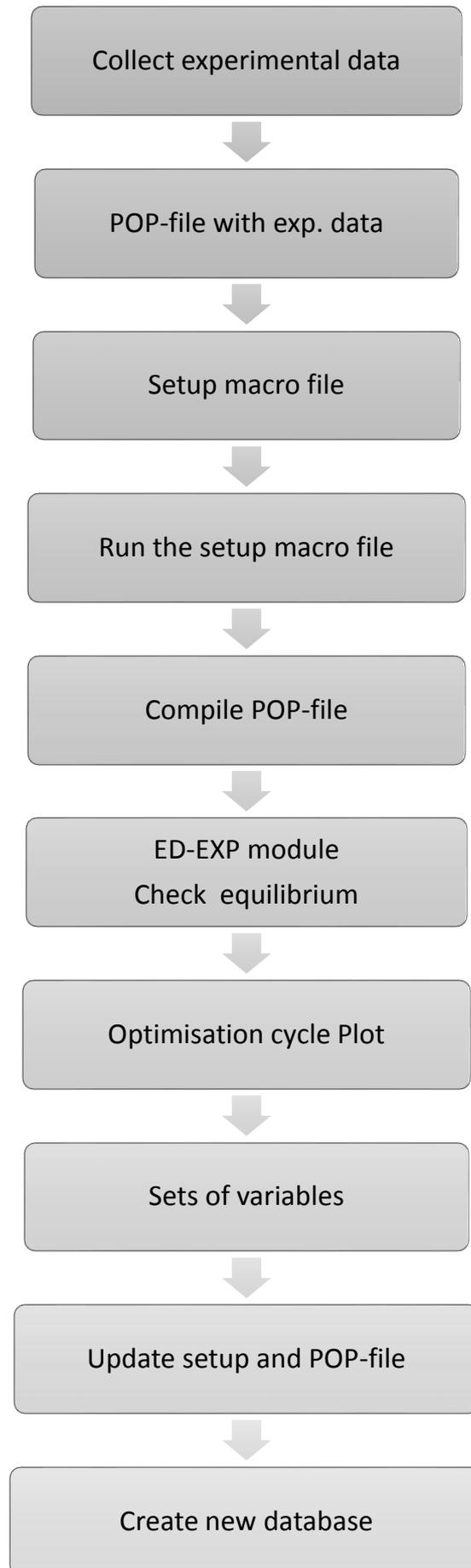
| | |
|-------------------------------|--|
| GO P-3 | PROLOG 1 |
| DEF-COMP | XSCALE 0.100000E-11 1.00000 |
| | YSCALE 0.416900E-12 1.00000 |
| C-S PHASE *=S | XTYPE LINEAR |
| C-S PHASE LIQUID=E 1 | YTYPE LINEAR |
| S-R-S CU LIQUID * 1E5 | XLENGTH 11.5000 |
| S-R-S BI LIQUID * 1E5 | YLENGTH 11.5000 |
| S-C N=1 P=1E5 T=1373 X(CU)=.5 | TITLE |
| C-E | XTEXT MOLE_FRACTION CU |
| S-A-V 1 X(CU) 0 1 0.005 | YTEXT ACR(BI) |
| STEP NORMAL | DATASET 1 |
| POST | CHAR 0.25 |
| S-D-A X M-F CU | COLOR 1 |
| S-D-A Y ACR(CU) | \$ BLOCK #306 1 FOR: |
| PLOT | \$E LIQUID |
| SET-INTERACTIVE | BLOCK X=C1; Y=C2; GOC=C3,WAD; |
| | \$ PLOTTED COLUMNS ARE : X(CU) and ACR(BI) |

Figure 6. Command lines for plotting activities in ThermoCalc

9. When you are satisfied with the fit between calculated results and experimental data with your final set of optimising variables, update your setup file and POP-file.

In the setup file, enter the calculated optimising variable values as the variables' start values. In the POP-file, enter the final weights of the experiments. With these files updated, you can easily regenerate the parameter values of your optimised system. Having the files updated also makes it easier to optimise the system again in light of new data or new theoretical models.

10. Finally, update the database with your calculated results or create a new database with information about the system that you have optimised.
[15]





6. Results and Discussion

6.1 Gibbs energies

The Gibbs energies of phases in the Cu-Bi system and the interaction parameters calculated in this work are shown in Table 1 for the corresponding temperature ranges.

Table 1

Gibbs energies of phases in the Cu-Bi system. Interaction Parameters

| Phase | T (K) | Function |
|----------------|---|---|
| Liquid | 298.15 - 544.55 | ${}^0G_{Bi}^{Liquid} = +GHSERBI\# + 11246.017 - 20.636399*T - 5.9608E-19*T^{**7}$ |
| | 544.55 - 800 | ${}^0G_{Bi}^{Liquid} = +40629.667 - 400.415652*T + 49.678*T*LN(T) - 0.0730245*T^{**2} + 1.3052833E-05*T^{**3} - 3544705*T^{**(-1)}$ |
| | 800 - 1200 | ${}^0G_{Bi}^{Liquid} = +250.689 + 162.14485*T - 36.041*T*LN(T) + 0.0074641*T^{**2} - 1.05047E-06*T^{**3} + 5175*T^{**(-1)}$ |
| | 1200 - 3000 | ${}^0G_{Bi}^{Liquid} = +3755.434 + 103.960336*T - 27.196*T*LN(T)$ |
| | 298.15 - 1357.77 | ${}^0G_{Cu}^{Liquid} = +GHSERCU\# + 12964.735 - 9.511904*T - 5.8489E-21*T^{**7}$ |
| | 1357.77 - 3200 | ${}^0G_{Cu}^{Liquid} = -46.545 + 173.881484*T - 31.38*T*LN(T)$ |
| | 298.15 - 3000 | ${}^0L_{Bi,Cu}^{Liquid} = +2.0155965E+04 - 6.2645507*T$ |
| 298.15 - 3000 | ${}^1L_{Bi,Cu}^{Liquid} = -2.8374171E+03 + 1.1518710*T$ | |
| 298.15 - 3000 | ${}^2L_{Bi,Cu}^{Liquid} = +5.9284900E+03 - 4.4122071*T$ | |
| Rhomboedral_A7 | 298.15 - 3000 | ${}^0G_{Bi}^{Rhombohedarl_A7} = +GHSERBI\#$ |

Where GHSERBI and GHSERCU are the Gibbs energies of elements in their reference state.

The ${}^iL_{Bi,Cu}^{Liquid}$ functions show the calculated parameters. Six different variables were used. As it can be seen, the final expression was $G_i(T) = a + bT$ due to the temperature independence shown in the results.

6.2 Phase Diagram

Figure 4 shows the calculated phase diagram of the binary system Cu-Bi superimposed with experimental data given by several authors [3, 4, 7, 19, 22–28]. The calculated liquidus line agrees well with the experimental data.

The phase diagram shows the liquidus line, which describes equilibrium of liquid alloy and solid copper phases, as obtained in this study, and experimental values from Taskinen et al. [9], Gomez et al. [19] and Nathans et al. [20] studies. The liquidus line from this study well represents location of the points obtained in experiments. Small discrepancy can be found for liquidus line, and the only significant divergence can be observed in the copper content range of 0.6–0.85. This type of misrepresentation in the experimentally determined liquidus line can result from the decrease of bismuth content in the examined alloy. In this range of concentrations and temperatures the process of bismuth vaporization is still intensive and has stronger effect on alloy composition when compared to the lower concentration of this element in the alloy and even higher temperatures

The assessed liquidus is in good agreement with the solubilities carefully measured by Nathans et al. [3], obtained by a static sampling technique over the whole concentration interval. The results are also in good agreement with the EMF data of Lomov et al. [25] and Taskinen et al. [19].

Eutectic point at $x_{\text{Cu}}=0.0037$ and $T=543.75$, 1K below melting point of pure bismuth. Nathans, $x_{\text{Cu}}=0.0048$ at $T=543.5$, Jeriomin $x_{\text{Cu}}=0.005$ ant $T\sim 543$.

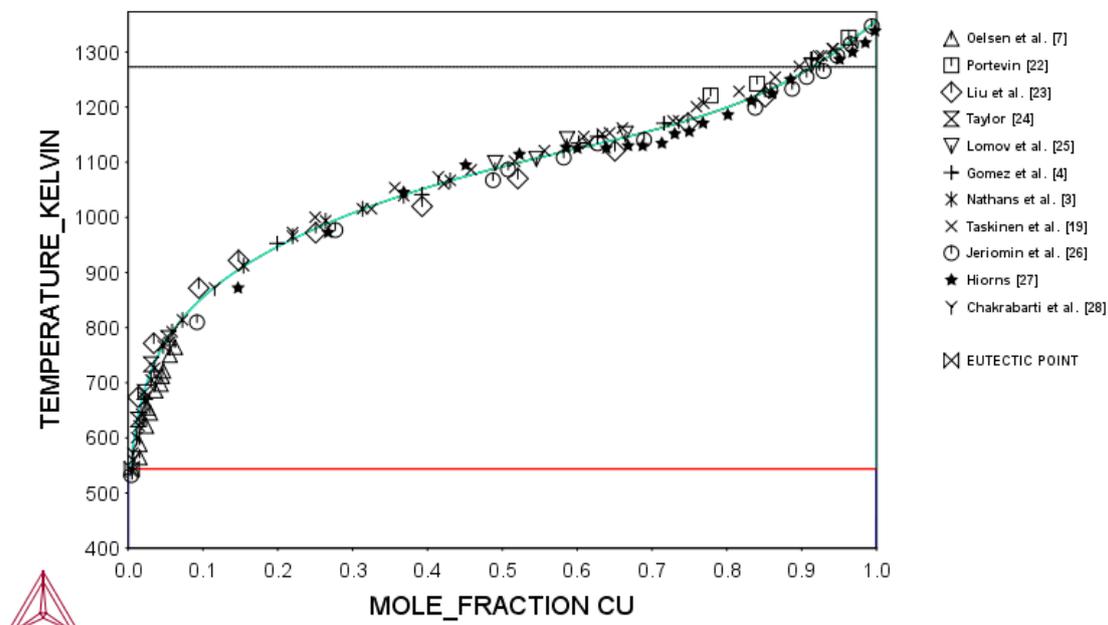


Figure 7. Phase diagram of the Cu-Bi system as calculated in this work superimposed to the experimental data by various authors.

6.3 Activities in liquid

Figure 5 shows the calculated activity of bismuth at 1200 K. It fits well to the experimental data offered by Hultgren and Nikolskaya, as well as the other authors [16, 17, 19] in their respective temperatures, with the exception of those reported by Itoh et al. [18]. These authors reported systematically too low bismuth activity values in copper-rich alloys at 1400 K by using a Knudsen effusion technique combined with an electrobalance.

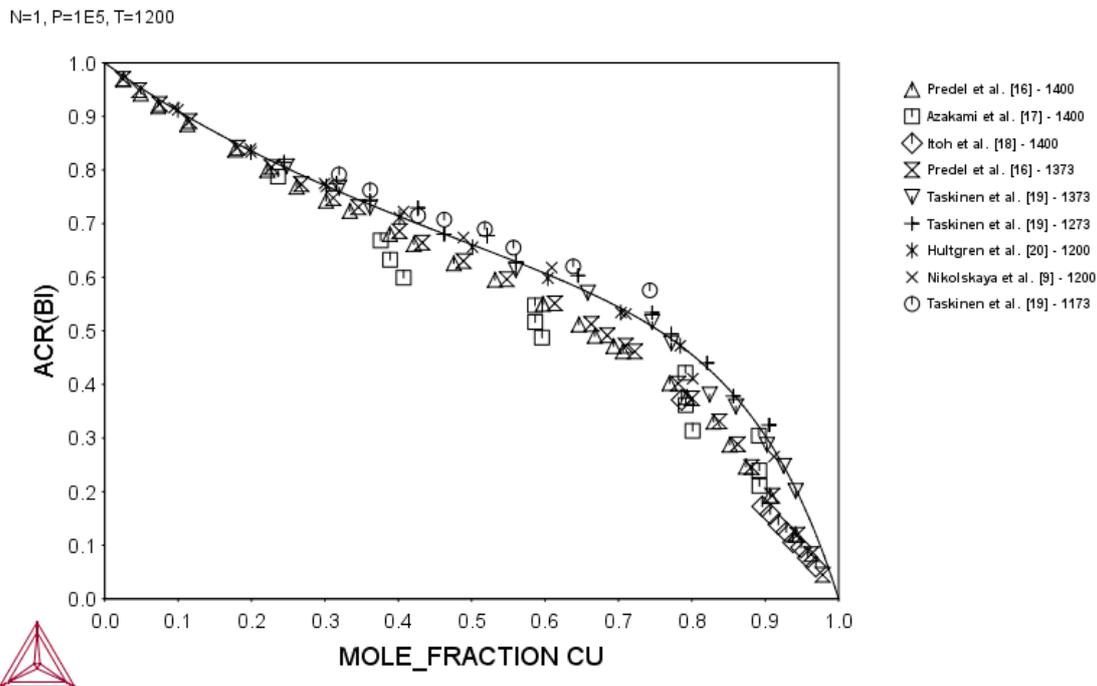


Figure 8. Activity of bismuth in molten copper as calculated in this work superimposed with the experimental data by multiple authors; standard state is Bi(l).

In Figure 6 is represented the activity of copper, function of the molar fraction of Cu. Not many experimental data is available, only the one given by Taskinen et al. [19] and Hultgren et al. [20]. The activity of copper calculated by Taskinen [19], as compared with the pure (hypothetical) CU(l), was carried out using the heat of fusion of copper, $L_{Cu}=13000$ J/mol, according to Kuba-Schewski et al. [29] and neglecting the contribution of heat capacity differences. The results show a good fit with the experimental data at both temperatures calculated, 1200 and 1373 K.

The limiting activity coefficients of bismuth in molten copper and copper in molten bismuth at infinite dilution are frequently needed in qualitative calculations for engineering purposes. Teppo et al. [5] give these coefficients in terms of the temperature.

N=1., P=1E5, T=1373

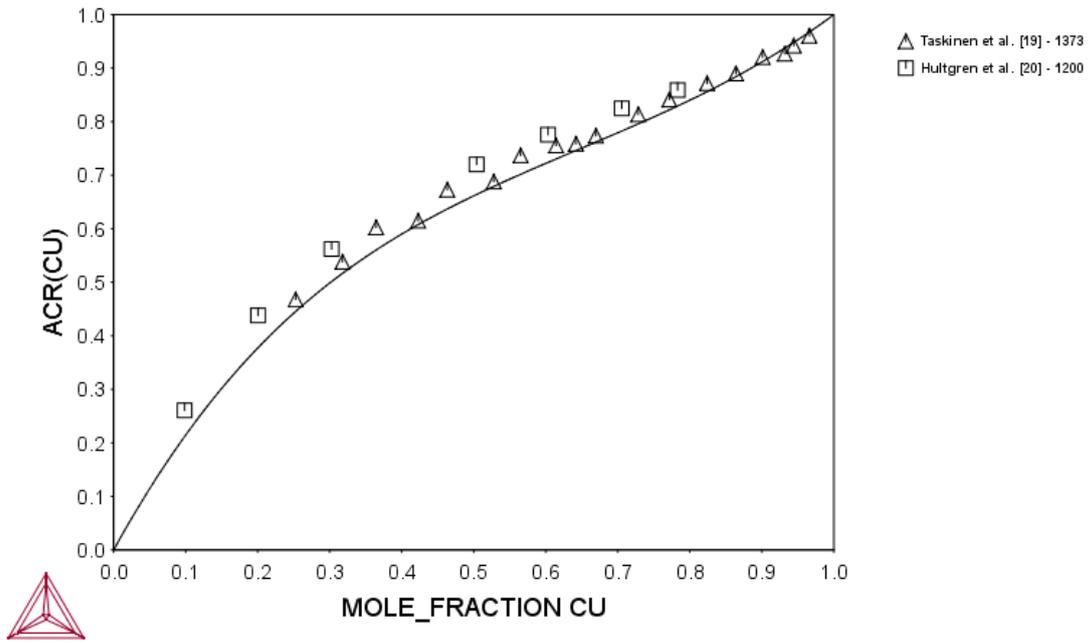


Figure 9. Activity of Cu in molten bismuth as calculated in this work superimposed with the experimental data by various authors; standard state is Cu(l).

6.4 Enthalpies of mixing

The integral enthalpies of mixing of liquid Bi-Cu alloys, relative to Bi(l) and Cu(l) standard states are endothermic and show negligible temperature dependence. Which is in full agreement with the studies by Niemelä et al. [10] and Teppo et al. [5]. The calculated ΔH^m curve, as shown in Figure 7, is nearly symmetrical, slightly shifted to the copper-rich side. There is a substantial scatter between the results of the different studies reported in the literature. Oelsen et al. [7] and Takeuchi et al. [21] have measured enthalpies of mixing calorimetrically at temperatures of 1416 K and 1369 K respectively. The present calculation also includes the values of the enthalpies of mixing selected by Hultgren et al. [20] and more recent studies by Flandorfer et al. [1], which measurements were carried out using a Calvet-type microcalorimeter and a drop calorimetric technique. The data was evaluated by means of a standard Redlich–Kister. This last set of experimental data shows a more symmetrical tendency of the enthalpies, but close to the present calculation. Flandorfer et al. [1] stated in their research that there is a slight but significant temperature dependence of ΔH^m in this system.

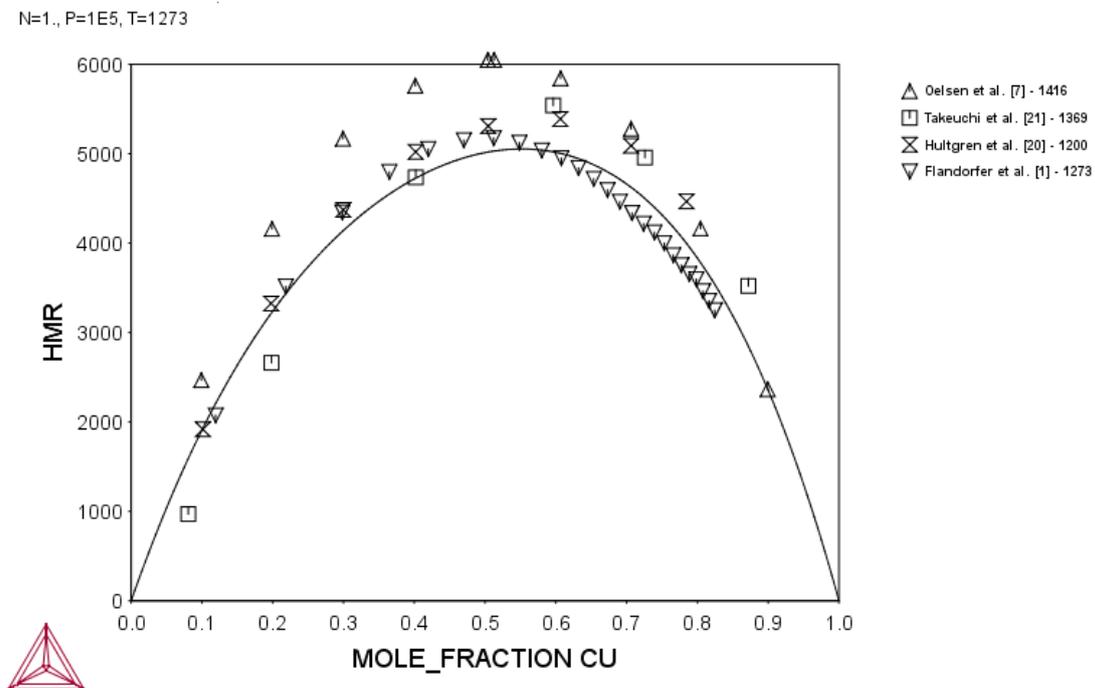


Figure 10. Integral enthalpies of mixing as calculated in this work superimposed with experimental data by various authors.



7. CONCLUSIONS

A new set of thermodynamic parameters was proposed for thermodynamic description of the binary copper-bismuth system. Calculations done by using available experimental data to obtain the new set of thermodynamic parameters. This set reproduce experimental data well, thus the thermodynamic database can be used as standalone description of the binary system as well as a part of description of higher-ordered systems.



8. References

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